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MONTBRAYITE, A NEW GOLD TELLURIDE

M. A. PEACOCK AND R. M. THOMPSON,
University of Toronto, Toronto, Canada.

ABSTRACT¹

Triclinic; $a=12.08$, $b=13.43$, $c=10.78$ kX, $\alpha=104^{\circ}30\frac{1}{2}'$, $\beta=97^{\circ}34\frac{1}{2}'$, $\gamma=107^{\circ}53\frac{1}{2}'$; partings, (110), (011), (111); (011):(111)= $41^{\circ}20'$, (111):(110)= $46^{\circ}45'$, (110):(011)= $69^{\circ}31'$. Fracture flat conchoidal. Very brittle. $H=2\frac{1}{2}$. $G=9.94$. Lustre metallic. Colour yellowish white. Polished sections white, moderately anisotropic, and homogeneous, except for inclusions of tellurbismuth, altaite, and petzite. Analysis by J. R. Williams: Au 44.32, Te 49.80, Bi 2.81, Pb 1.61, Sb 0.90, Ag 0.55, Fe trace; total 99.99. Cell content near $12[Au_2Te_3]$. Strongest x -ray powder lines: 2.97 kX (8), 2.92 (8), 2.08 (10), 1.717 (2), 1.699 (2). Embedded with gold, tellurbismuth, altaite, petzite, melonite, chalcopyrite, pyrite, sphalerite, chalcocite, and marcasite, in the Robb-Montbray mine, Montbray township, Abitibi County, Quebec.

The mineral described in this paper is an arresting constituent of the rich masses of tellurides, sulphides, and free gold produced by the Robb-Montbray mine in Montbray township, Abitibi County, Quebec, during the period 1925–28. The history and geology of this group of prospects, which produced spectacular specimen material but no commercial quantity of ore, is described by Cooke, James & Mawdsley (1931, pp. 224–227). The late Professor Ellis Thomson (1928) gave a mineralographic description of a suite of specimens, and we have recently described melonite from the same locality (1946b). The present paper is concerned mainly with the specific properties of the new gold telluride for which we have proposed the name *montbrayite* (1945, 1946a).

Mr. H. S. Wilson, consulting geologist at Bourlamaque, Quebec, has been kind enough to send us some notes based on his recollection of the discovery of the rich ore. From these notes the high-grade pocket of gold and tellurides was a flat mass, perhaps six feet in length, three to four feet in width, and from one to two inches thick, which occupied a tensional fracture on one wall of a nearly vertical, partly gouge-filled slip between the first and second levels of the mine. The material at our disposal consisted of several fine specimens generously presented by

¹ Improving in some details the previously published abstracts (Peacock & Thompson, 1945, 1946a).

R. A. Bryce, Esq., President of the Macassa Mines Limited, and Dr. M. H. Froberg, of the same company, and two handsome specimens, M 15815 and M 19883, kindly lent for study from the Royal Ontario Museum of Geology and Mineralogy by Dr. V. B. Meen. The first of these museum specimens comprised a dozen pieces representing the material which had been studied and described by Thomson (1928), while the second is perhaps the largest piece of the ore that has been preserved (500 gm.).

Physical and microscopical characters. The pieces of telluride ore are compact coarsely crystalline masses of metallic minerals almost wholly free from gangue, mostly somewhat tabular in shape, 1–2 cm. thick and up to 12 cm. wide. The broad surfaces which were apparently in contact with the wall-rock, are often dull and pitted and partially coated with a bluish-gray flour-like material which gave an x-ray powder photograph that could not be identified. Some of these surfaces are also encrusted with considerable amounts of coarse sponge and wire gold. Freshly broken surfaces show coarsely crystallized aggregates of metallic minerals, tellurbismuth (Bi_2Te_3), altaite (PbTe), montbrayite (Au_2Te_3), petzite (Ag_3AuTe_2), melonite (NiTe_2), and gold, with chalcopyrite, pyrite, sphalerite, chalcocite, and marcasite, all of which were definitely identified by physical, chemical, microscopical, and röntgenographic methods. Referring to the description by Thomson (1928), which was written in the earlier days of mineralography, it is clear that his "tetrady-mite" is tellurbismuth and his "krennerite" is the new montbrayite; pyrrhotite and a single example of coloradoite were mentioned by Thomson but not observed by us, while we have found small amounts of melonite and marcasite which were not noted by Thomson.

The gold telluride is abundant in some specimens, forming equidimensional masses sometimes exceeding 1 cm. in diameter. Occasionally such masses show perfect but interrupted planes of separation extending the full width of the mass and proving that it is structurally continuous. This appearance of a perfect cleavage, together with the general physical and chemical properties, at once suggest krennerite, but closer study showed that our mineral cannot be identified with that species.

Montbrayite has a splendid metallic lustre and a yellowish-white colour which is slightly lighter than that of calaverite. The mineral is very brittle and it breaks with a flat conchoidal fracture. The hardness is $2\frac{1}{2}$ and the specific gravity is 9.94, which is the average of values ranging from 9.90 to 9.98 obtained on seven fragments measured separately on the Berman balance. This specific gravity is distinctly higher than that of any similar mineral and it was this property that first suggested a closer study of the gold telluride.

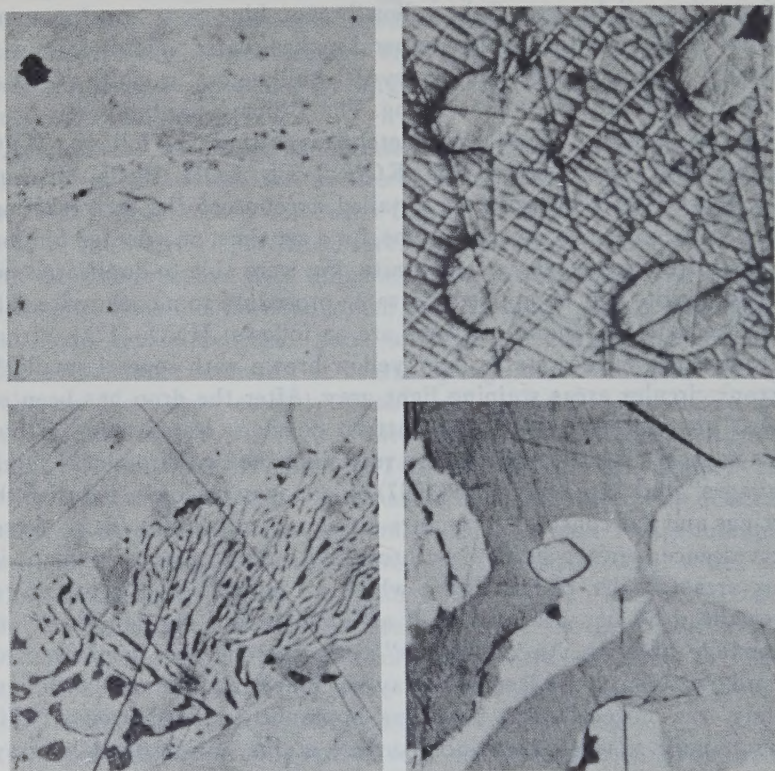
Montbrayite polishes to a smooth homogeneous surface which is creamy white in reflected light, like the colour of krennerite, and distinctly less white than altaite (Figs. 1, 3). Reflection pleochroism is rarely perceptible and the anisotropism is weak to moderate with polarization colours light gray, light yellow-brown, blue-gray, varying somewhat with the orientation. The mineral makes coarse solid mosaics with optically continuous areas often several millimeters in width. Crossed nicols reveal no evidence of twinning. The Talmage hardness is C.

The reactions to the standard etch-reagents are as follows: HNO_3 positive with effervescence; HCl , KCN , FeCl_3 , KOH , HgCl_2 , all negative. Short (1937) has given a detailed account of the etch-reactions with HNO_3 in various concentrations, for a set time, on oriented sections of calaverite, krennerite, and sylvanite. We were able to duplicate some of these results and we applied the same procedure to montbrayite. The etch-reactions on random sections are as follows: HNO_3 (1:1), strong effervescence; surface stains light yellow-brown with several small (50 micron) circular areas staining light gray. After the drop has been removed an "alligator-skin" etch-pattern develops leaving the circular areas in relief (Fig. 2). This pattern resembles the two-directional "etch-cleavages" illustrated by Short (1937), and it may be connected with the partings and flat conchoidal fracture of the mineral. HNO_3 (3:2), slower effervescence; surface stains light brown with development of small circular areas similar to the above which are also stained light brown. After the drop has been removed an etch-pattern develops with one prominent direction. An "epidermis" a few microns thick tends to come off and curl up at the edges; this may be completely removed with hard buffing, the surface again becoming apparently homogeneous. HNO_3 (conc.), very slow effervescence; surface stains uniformly light gray-brown. No etch-pattern develops after the drop has been removed; circular areas are absent.

The relatively unetched or little etched circular areas in montbrayite are similar to those described by Short in krennerite and calaverite, and it is natural to suppose that they are areas that differ in some way, perhaps very slightly, from the surrounding mineral. The areas are not distinguishable on an unetched surface and they are too small to be sampled for separate tests. Comparing all the microscopic characters of montbrayite with those of krennerite and calaverite it will be seen that there is little prospect of definitely distinguishing the three minerals by ordinary mineralographic methods.

The following minerals are found in contact with montbrayite or enclosed within the gold telluride: altaite, tellurbismuth, petzite, gold, chalcopryrite, and melonite (Figs. 1-4). Altaite, with small amounts of

gold and petzite, occurs in thin stringers cutting montbrayite (Fig. 1). Tellurbismuth with subordinate altaite and small patches of petzite make ovoid inclusions with a eutectoid structure, irregularly distributed



FIGS. 1-4. Montbrayite and associated minerals: polished sections in ordinary reflected light. Fig. 1. Homogeneous montbrayite traversed by a veinlet of altaite containing particles of gold and petzite. $\times 92$. Fig. 2. Montbrayite etched with 1:1 HNO_3 for 40 seconds, showing "alligator-skin" etch-pattern and relatively little etched rounded areas in relief. $\times 197$. Fig. 3. Ovoid inclusion of tellurbismuth (light gray), altaite (dark gray), and petzite (medium gray), in montbrayite; tellurbismuth and altaite show eutectoid relations; etched with HCl . $\times 92$. Fig. 4. Subhedral crystal of melonite, with relief, in contact with montbrayite (light gray) and petzite (dark gray); the light gray areas to the right and below are gold. $\times 92$.

through montbrayite (Fig. 3). In total bulk these inclusions might amount to 10 per cent of the montbrayite and in some cases they reach 1 mm. in diameter. In ordinary light the altaite shows as straight or

curved bluish white bands within the tellurbismuth, which is faintly reddish white by contrast and not easily distinguished from the surrounding montbrayite. Crossed nicols emphasize the anisotropic tellurbismuth, and staining with HCl darkens the bands of altaite (Fig. 3). These inclusions have the appearance of exsolution products. Petzite occurs as irregular areas often surrounding and traversing patches of montbrayite, and occasionally cutting altaite, tellurbismuth and melonite. Subhedral hexagonal crystals of melonite, with or without partial rims of petzite, occur in montbrayite, but the best crystal outlines are shown by isolated plates of melonite in altaite. The chalcopyrite does not occur in the montbrayite itself but at the boundaries of altaite, tellurbismuth, petzite, and gold with montbrayite.

Crystallography. In the compact ore masses the gold telluride had no chance to develop a crystal form, but the plane separation surfaces developed on some broken masses and fragments offered an opportunity for crystallographic measurements. To discover whether a separation plane corresponds to the basal cleavage of krennerite, or the side-pinakoidal cleavage of sylvanite, a fragment was rotated about the normal to one of these mirror-like surfaces to give a rotation photograph. The picture was that of a single crystal in random orientation, showing that the gold telluride is not structurally similar to krennerite or to sylvanite, or to calaverite, which has no cleavage.

Among many fragments examined a few were found with two planes of separation meeting in an edge. Measurements of the interfacial angles on a dozen fragments gave three different angles, indicating that there are in fact three planes of separation, all of which were eventually found on a single fragment. The three planes of separation, *A*, *B*, *C*, gave good to excellent reflections and the following quite consistent interfacial angles on the reflecting goniometer:

$$BC = 41^{\circ}17' - 41^{\circ}32' \text{ (3); weighted average } 41^{\circ}20'$$

$$CA = 46^{\circ}42' - 46^{\circ}48' \text{ (4); weighted average } 46^{\circ}45'$$

$$AB = 69^{\circ}30' - 69^{\circ}34' \text{ (5); weighted average } 69^{\circ}31'$$

These planes of separation are unlike crystal cleavages in several respects: they occur only on limited parts of broken surfaces and on the minority of broken fragments; they can rarely be developed at will; they sometimes pass in a curious way from a perfect plane into a warped fracture surface; and finally, the planes do not have the simplest symbols in the crystal lattice. The planes are therefore partings, rather than difficult cleavages, as given in the recent abstract (1945, 1946a). The possibility that two of these partings, or all three, might be crystallographi-

cally equivalent was constantly kept in mind, but no alternative was found to the conclusion that each is parallel to a different set of planes in a triclinic lattice.

Rotation photographs were taken with copper radiation on parting fragments turning around each of the three parting-edges, and Weissenberg resolutions were made of the zero and first layers about the edges C/A and A/B . The Weissenberg photographs were unusual in showing a relatively small number of unsystematically distributed strong spots while the remaining spots, including the rows from the parting planes, were quite faint. The projections gave asymmetric reciprocal lattice nets, offset on the first layers, indicating a triclinic lattice.

The most accurate lattice constants were considered to be the spacings of the parting planes and provisional axial planes $d(A)$, $d(B)$, $d(C)$, measured on the zero-layer Weissenberg photographs, and the interplanar angles BC , CA , AB , measured on the reflecting goniometer and verified on the Weissenberg photographs. From these constants the dimensions of a preliminary simple triclinic cell, a' , b' , c' , α' , β' , γ' , were calculated and the cell edges thus obtained were closely verified by values for a' , b' , c' , measured on the three rotation photographs.

From zero-layer Weissenberg photos	Calculated	From rotation photos
$d(A) = 10.24 \text{ kX}$	$a' = 14.96 \text{ kX}$	$a' = 14.98 \text{ kX}$
$d(B) = 9.34 \text{ kX}$	$b' = 15.05 \text{ kX}$	$b' = 15.06 \text{ kX}$
$d(C) = 7.41 \text{ kX}$	$c' = 15.36 \text{ kX}$	$c' = 15.42 \text{ kX}$
$BC = 41^\circ 20'$	$\alpha' = 138^\circ 30\frac{1}{2}'$	
$CA = 46^\circ 45'$	$\beta' = 133^\circ 03\frac{1}{2}'$	
$AB = 69^\circ 31'$	$\gamma' = 70^\circ 00'$	
	$V' = 1567.9 \text{ kX}^3$	

This preliminary cell, shown with broken lines in Fig. 5, is unconventional since its edges are not the shortest lattice periods. The conventional cell, whose edges a , b , c , are the three shortest non-coplanar lattice

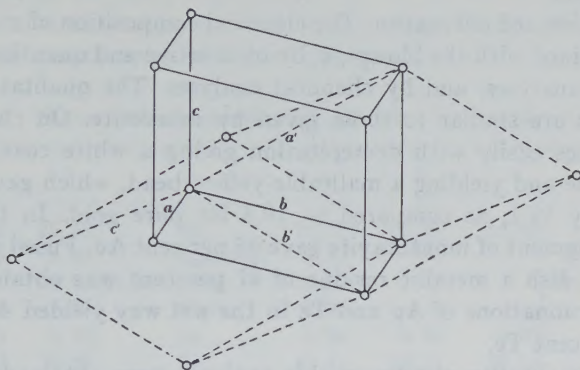


FIG. 5. Montbrayite: crystal lattice, showing the preliminary cell $a'b'c'$ and the conventional cell abc which are related by the transformation, preliminary to conventional: $10\bar{1}/111/01\bar{1}$.

periods, oriented with $c < a < b$, α and β obtuse, is related to the preliminary cell by the reversible transformations:

Preliminary to Conventional: $10\bar{1}/111/01\bar{1}$

Conventional to Preliminary: $011/110/\bar{1}\bar{1}\bar{1}$

By calculation, the dimensions of the conventional cell are:

$$a=12.08, b=13.43, c=10.78 \text{ kX}, \alpha=104^\circ 30\frac{1}{2}', \beta=97^\circ 34\frac{1}{2}', \gamma=107^\circ 53\frac{1}{2}'.$$

The volume of this cell is 1568.0 kX^3 , in agreement with the volume of the preliminary cell, 1567.9 kX^3 . The complete geometrical elements of the conventional cell are:

$$\begin{aligned} a:b:c &= 0.8998:1:0.8026; \alpha=104^\circ 30\frac{1}{2}', \beta=97^\circ 34\frac{1}{2}', \gamma=107^\circ 53\frac{1}{2}' \\ p_0:q_0:r_0 &= 0.9074:0.8360:1; \lambda=72^\circ 02', \mu=76^\circ 54\frac{1}{2}', \nu=69^\circ 14' \\ p_0' &= 0.9623, q_0' = 0.8866, x_0' = 0.1329, y_0' = 0.3272. \end{aligned}$$

With reference to the conventional cell, the parting planes become $A(\bar{1}10)$, $B(0\bar{1}\bar{1})$, $C(\bar{1}\bar{1}\bar{1})$, or their parallel opposites, $A'(\bar{1}\bar{1}0)$, $B'(0\bar{1}\bar{1})$, $C'(\bar{1}\bar{1}\bar{1})$, while the parting edges become $B/C=B'/C'=[011]$, $C/A=C'/A'=[110]$, $A/B=A'/B'=[\bar{1}\bar{1}\bar{1}]$. Thus none of the three sets of plane separations are among the three sets of lattice planes with the greatest spacings, and none of the three resulting edges are among the three shortest lattice periods. If the plane separations were true cleavages these conditions would be contrary to all previous experience. But

parting planes, which might in the present case be planes of weakness due to stress accompanying a structural change in the solid state, need not be subject to the same conditions that govern normal planes of least cohesion.

Composition and cell content. The chemical composition of montbrayite was determined with the blowpipe, by qualitative and quantitative spectrographic analyses, and by chemical analyses. The qualitative pyrognostic tests are similar to those given by calaverite. On charcoal the mineral fuses easily with decrepitation giving a white coating of tellurium oxide and yielding a malleable yellow bead, which gave the specific gravity 19.1, as compared to 19.3 for pure gold. In this way a weighed fragment of montbrayite gave 45 per cent Au. Fused with borax in an open dish a metallic residue of 47 per cent was obtained. Semi-micro determinations of Au and Te in the wet way yielded 44 per cent Au, 48 per cent Te.

Several qualitative spectrographic analyses were obtained; the most complete of these was kindly made under the direction of Dr. G. R. Harrison (Massachusetts Institute of Technology), who reported that two samples of the gold telluride are qualitatively identical, with the major constituents, Au, Pb, Te, Bi, Ni, Sb, Ag; minor constituents, Mg, Si, Fe, Cu, Ca; and traces of Sn, Na, K, Al.

A quantitative spectrographic analysis of montbrayite was kindly made by Dr. J. C. Rabbitt, in the Department of Mineralogy and Petrography, Harvard University, with the following percentage results:

Au	Sb	1.0 ±0.1	Ti	0.02 ±0.002	
Te	Ni	0.6 ±0.06	Co	0.01 ±0.001	
Bi	2.5±0.3	Ag	0.5 ±0.05	Cu	0.008±0.0008
Pb	1.5±0.2	Fe	0.02±0.002	Mo, Sn, Cr, V	<0.001

Finally a chemical analysis was made by J. R. Williams (Vancouver, British Columbia) on 0.6 gm. of the cleanest available material. From the polished sections, and the appearance of the fragments of this sample, it was clear that inclusions of the eutectoid intergrowth of tellurbismuth and altaite could not be avoided and that small amounts of petzite might also be contained in the analyzed material; but there was no indication that the sample was contaminated by significant amounts of the other associated minerals.

The chemical analysis and a discussion of the results are given in Table 1. If it is assumed that the reported elements (1) all belong to montbrayite the cell content (2) is obtained. This content approaches $12[\text{Au}_2\text{Te}_3]$ with Au partly replaced by Ag, Pb, Bi, Sb; but this interpretation cannot strictly apply at room temperature, in view of the observed inclusions in montbrayite. A better interpretation of the analysis is ob-

TABLE 1. MONTBRAYITE: ANALYSIS AND CELL CONTENT

	1	2		3	4	5	6
Au	44.32	21.23	Au	43.99	48.50	23.66	50.77
Ag	0.55	0.48	Ag_3AuTe_2	1.32	—		
Pb	1.61	0.73	PbTe	2.60	—		24.44
Bi	2.81	1.27	Bi_2Te_3	5.38	—		
Sb	0.90	0.70	Sb	0.90	0.99	0.78	
Te	49.80	36.89	Te	45.81	50.51	38.12	49.23
	99.99			100.00	100.00		100.00

1. Analysis of material with visible inclusions of tellurbismuth (Bi_2Te_3), altaite (PbTe), and petzite (Ag_3AuTe_2), by J. R. Williams.

2. Atoms in unit cell with $V=1568 \text{ kX}^3$, $G=9.94$.

3. Analysis recast to give Ag_3AuTe_2 , PbTe , Bi_2Te_3 , and $\text{Au}+\text{Sb}+\text{Te}$ for montbrayite.

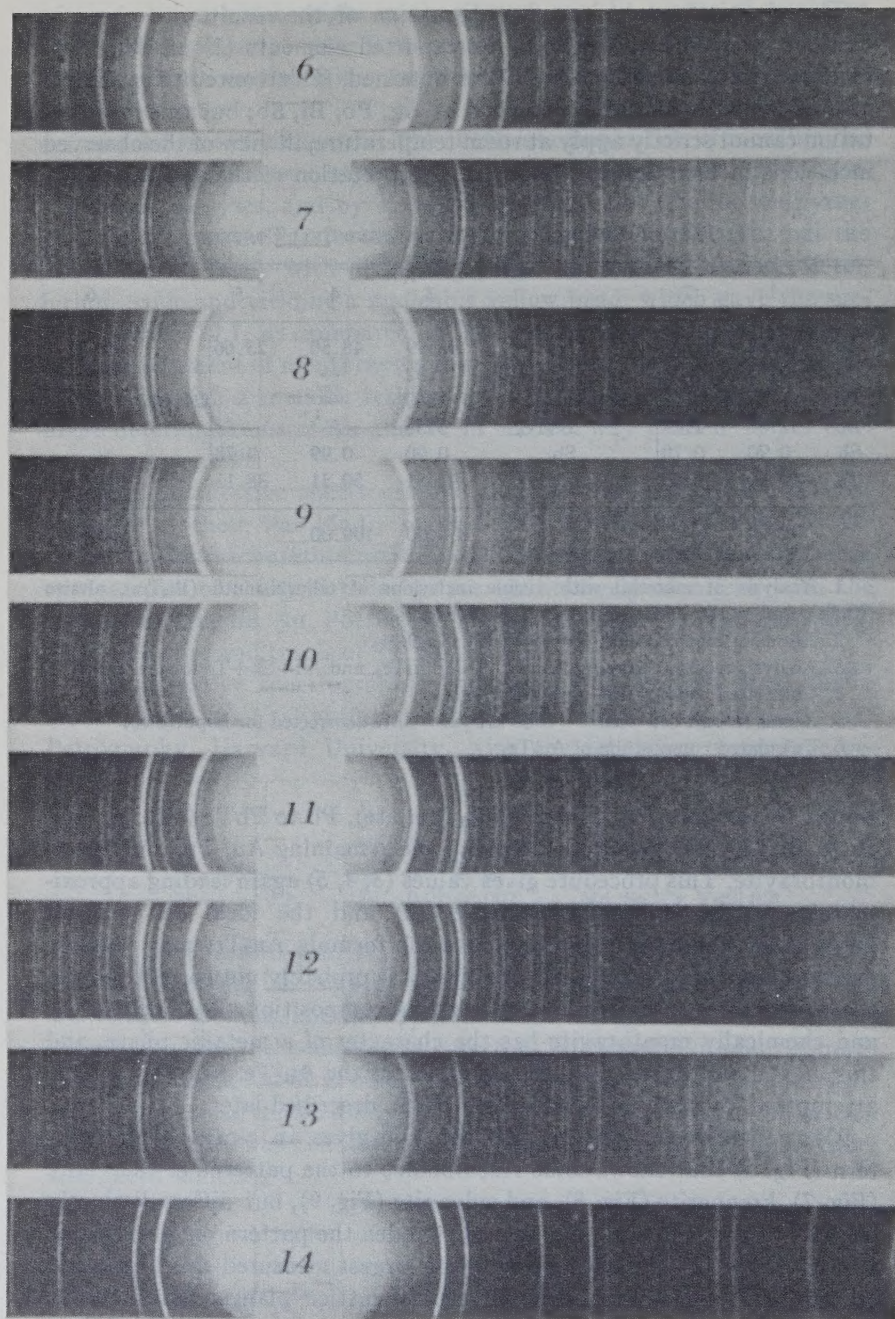
4. Calculated composition of montbrayite.

5. Atoms in unit cell with $V=1568 \text{ kX}^3$, $G=10.13$ (corrected for impurities).

6. Calculated composition of Au_2Te_3 .

tained by assigning Ag to Ag_3AuTe_2 (petzite), Pb to PbTe (altaite), and Bi to Bi_2Te_3 (tellurbismuth), leaving the remaining Au, Te, and Sb, to montbrayite. This procedure gives values (3, 4, 5) again leading approximately to the composition Au_2Te_3 (6) and the ideal cell content $12[\text{Au}_2\text{Te}_3]$. For descriptive purposes the formula Au_2Te_3 may then be used for montbrayite; at the same time it is probably not correct to infer the existence of a true compound of this composition. Both physically and chemically montbrayite has the character of a metallic phase, and this view is supported by a consideration of the Au-Te diagram and the attempts to prepare artificial montbrayite, described later.

X-ray powder photographs. Montbrayite gives an x -ray powder pattern (Fig. 6) that shows some resemblance to the patterns of calaverite (Fig. 7), krennerite (Fig. 8), and sylvanite (Fig. 9), but differs distinctly from all of them. It was impractical to index the pattern on the triclinic lattice, owing to the fact that even the largest measured spacings could be referred to numerous different sets of lattice planes; but the relatively simple pattern made by the more prominent lines or pair of lines



can be indexed and approximately matched by spacings in a cubic lattice with $a = 4.16$ kX (Table 2). This cubic lattice is apparently not a regular

TABLE 2. MONTBRAYITE: X-RAY POWDER PHOTOGRAPH
Pseudocubic; $a = 4.16$ kX

<i>I</i>	θ (Cu)	<i>d</i> (meas.)	(<i>hkl</i>)	<i>d</i> (calc.)	<i>I</i>	θ (Cu)	<i>d</i> (meas.)	(<i>hkl</i>)	<i>d</i> (calc.)
1	5.9	7.48	—	—	$\frac{1}{2}$	24.75	1.836	—	—
2	9.9	4.47	—	—	$\frac{1}{2}$	25.5	1.786	—	—
$\frac{1}{2}$	10.9	4.07	—	—	2	26.6	1.717	—	—
$\frac{1}{2}$	11.65	3.81	—	—	2	26.9	1.699	(112)	1.698
$\frac{1}{2}$	12.6	3.52	—	—	2	31.05	1.490	—	—
1	13.8	3.22	—	—	2	31.8	1.459	(022)	1.471
8	15.0	2.97	(011)	2.942	$\frac{1}{2}$	32.2	1.443	—	—
8	15.25	2.92			$\frac{1}{2}$	33.5	1.393	{(003)} {(122)}	1.387
$\frac{1}{2}$	18.1	2.47	—	—	$\frac{1}{2}$	35.05	1.339	—	—
1	18.9	2.37	(111)	2.402	1	35.55	1.322	(013)	1.315
1	19.75	2.27	—	—	2	35.95	1.309		
1	21.3	2.12	—	—	$\frac{1}{2}$	39.4	1.211	—	—
10	21.65	2.08	(002)	2.080	2	39.9	1.198	(222)	1.201
1	22.2	2.03	—	—	1	47.6	1.041	(004)	1.040
1	22.9	1.975	—	—	$\frac{1}{2}$	55.1	0.937	(024)	0.930
1	23.8	1.905	—	—	1	56.1	0.926		
$\frac{1}{2}$	24.45	1.857	(012)	1.860					

pseudocell of montbrayite, since its volume is not a simple aliquot part of the true cell; it may, however, represent a nearly cubic arrangement of the heaviest (Au) atoms, and it suggests that montbrayite may have originated by inversion in the solid state from a cubic high temperature phase. In this way a pseudocubic arrangement might be preserved, while the inversion to the lower, in this case triclinic, symmetry, might result in stresses which could cause the partings in the mineral.

Fusion experiments. The Au-Te diagram as given in Hansen (1936, p. 264), shows only one compound, AuTe₂ (calaverite, 56.4% Te by weight), which has no solid-solution range. This compound makes a eutectic with Au at 42% Te and a eutectic with Te at 82.5% Te. At 50% Te, corresponding to the composition of montbrayite, a melt would

FIGS. 6-14. X-ray powder photographs with Cu radiation, Ni filter; camera radius, $90/\pi$ mm. ($1^\circ\theta = 1$ mm.); full size reproductions of contact prints. Fig. 6. Montbrayite, Montbray township, Quebec. Fig. 7. Calaverite, Cripple Creek, Colorado. Fig. 8. Krennerite, Cripple Creek, Colorado. Fig. 9. Sylvanite, Nagyág, Hungary. Fig. 10. Fused montbrayite, giving the patterns of calaverite and gold. Fig. 11. Fusion with the composition of the analysis of montbrayite, giving the patterns of calaverite and gold. Fig. 12. Fusion with the composition Au:Te=2:3, giving the patterns of calaverite and gold. Fig. 13. Calaverite. Fig. 14. Gold.

first give crystals of AuTe_2 and finally solidify as a mixture of AuTe_2 and Au.

Some fusion experiments, with weighed amounts of the powdered elements in evacuated silica glass tubes, gave results in keeping with previous work. Mixtures corresponding to the analysis of montbrayite, and to the idealized composition Au_2Te_3 , gave two-phase products whose powder patterns (Figs. 11, 12) are alike and consist of combinations of the pattern of calaverite (Fig. 13) and of gold (Fig. 14). Fragments of montbrayite heated under like conditions first shattered and then fused to give similar intergrowths of calaverite and gold (Fig. 10). This showed, as was expected, that montbrayite will not form under fusion conditions, and that the mineral represents an unstable phase formed under less drastic natural conditions. In this respect montbrayite resembles krennerite and sylvanite, neither of which we were able to reproduce under fusion conditions. An even closer analogy exists between montbrayite and the recently described new bismuth telluride, hedleyite (Warren & Peacock, 1945), which breaks down into Bi and a solid solution of Bi in Bi_2Te_3 on fusion and recrystallization in vacuum.

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MANGANESE AND LEAD AS COACTIVATORS OF RED FLUORESCENCE IN HALITE*

K. J. MURATA AND ROBERT L. SMITH.**

ABSTRACT

The bright red fluorescence of some halite from California dry lake deposits and from a salt spring in Idaho is due to coactivation by minute amounts of manganese and lead. Neither manganese nor lead alone activates the red fluorescence. Chemical, spectrographic, and synthetic experiments, which identify manganese and lead as coactivators and throw light on the mode of precipitation of these elements by growing halite crystals, are described. The marked preferential coprecipitation of lead by growing halite crystals results in zonation of fluorescence in crystals and restriction of fluorescence to the first crops of crystals, when the supply of lead is limited.

INTRODUCTION

While treating specimens of the natrolite rock from San Benito County, California, with hydrochloric acid in order to free crystals of enclosed neptunite, the junior author noticed that the halite obtained by evaporation of the resulting solution fluoresced red¹ under the ultra-violet lamp (Mineralight). This showed that it was feasible to synthesize red-fluorescing salt from water solutions, once the element activating the fluorescence was identified, and further suggested that an explanation might be found for the red fluorescence of halite from two localities in California and from a locality in Idaho.

When examined with a small Welch grating spectroscope, the fluorescent light of halite from these localities as well as of the salt crystals that had been accidentally prepared was the same—a continuous spectrum extending from green to red, faint in green and yellow and progressively stronger in orange and red. This spectrum was strikingly similar to that of the well known red-fluorescing calcite from Franklin, New Jersey, for whose fluorescence manganese has been found to be essential.²

A simple experiment soon showed that red-fluorescing halite could be obtained readily from a sodium chloride solution to which a small amount of manganous chloride or sulfate had been added.

* Published by permission of the Director, Geological Survey, U. S. Department of the Interior, Washington, D. C.

** On military leave.

¹ The fluorescence color of the natural and synthetic halite specimens examined during the course of our study included various tints of red. Most specimens fluoresced a deep pink. However, the term red seems preferable to pink because red has been used in all previous descriptions of this fluorescence in the literature.

² Brown, W. L., *Univ. Toronto Studies*, Geol. Ser. no. 36, 45-54 (1934).

Fonda, G. R., *Jour. Phys. Chem.*, 44, 435-439 (1940).

A spectrographic analysis of the sodium chloride crystals derived from natrolite showed 0.3 per cent of Mn, besides small amounts of other common elements such as magnesium, iron, aluminum, and calcium, and, in addition, a trace of lead. The natural halite samples were also found spectrographically to contain manganese, but in extremely small concentrations. They also contained traces of lead, the significance of which will be discussed later in the paper.

PREVIOUS WORK

During the course of his extensive study of the effect of radium rays on minerals, Przibram³ noted that some drusy (secondary?) halite from Stassfurt fluoresced red when exposed to radium rays. Jahoda⁴ investigated this material further and concluded from results of chemical analyses and synthetic experiments that the red fluorescence was due to small amounts of manganese (0.1–0.01% Mn) in the halite. He prepared a manganiferous salt for comparisons with the Stassfurt halite both by fusion methods and by crystallization from water solutions.

Oka and Yagi,⁵ while studying the effect of various heavy metal ions in promoting the formation of clear sodium chloride crystals from water solutions, noted that crystals obtained from solutions to which small amounts of manganous chloride had been added fluoresced red under ultraviolet light. Randall⁶ examined a large number of luminescent compounds that are activated by manganese, and described the cathodoluminescence spectrum of a synthetic sample of manganiferous sodium chloride prepared by heating a mixture of sodium chloride and a small amount of a manganese salt to 747°C.

The red fluorescence of sodium chloride, therefore, has been related to its content of manganese by several investigators. Our contribution to the subject will consist in proving that our samples from California and Idaho are additional examples of such an activation, and also in describing some new observations on a hitherto unsuspected role that lead plays in this manganese-activated fluorescence of halite.

The various aspects of our study will be discussed more or less in the order that they were investigated. This procedure allows us to discuss the different properties of red-fluorescing halite in a logical way, and also

³ Przibram, Karl, *Akad. Wiss. Wien, math.-naturwiss. Kl., Sitzungsber., Abt. IIa*, **134**, 234–235 (1925).

⁴ Jahoda, Eduard, *Idem*, **135**, 675–703 (1926).

⁵ Oka, Sojiro, and Yagi, Sakaye, *Jour. Soc. Chem. Ind. Japan*, Supplem. Binding, **36**, 143B–144B (1933).

⁶ Randall, J. T., *Proc. Roy. Soc. London*, ser. A, **170**, 272–293 (1939).

serves to emphasize the power of spectrographic methods in the study of fluorescent minerals that are activated by trace elements.

LOCALITIES

Halite from primary marine rock salt deposits of Carlsbad, New Mexico; Grand County, Utah; Detroit, Michigan, and Retsof, New York, does not fluoresce. Reagent-grade sodium chloride, spectrographically free of manganese but containing traces of lead, is likewise non-fluorescent. The three known American localities that yield red-fluorescing halite are a desert lake deposit near Amboy, California,⁷ a similar deposit in Borego Valley, San Diego County, California,⁸ and the Petersen salt spring⁹ in the valley of Tygee Creek, Idaho, 3.5 miles west of Auburn, Wyoming.

The dry lake salt deposit near Amboy, California, has been briefly described by Phalen.¹⁰ It was mined during World War II to furnish salt for the plant producing magnesium at Las Vegas, Nevada. It would be of great interest to examine the deposit with an ultraviolet lamp at night in order to ascertain the mode of distribution of the red-fluorescing salt. The dry lake deposit of Borego Valley, San Diego County, California, apparently has not yet been described.

The brine spring in eastern Idaho, whose salt was found by us to fluoresce red, is believed by Mansfield¹¹ to owe its origin to circulating ground water coming in contact with beds of rock salt in the Jurassic sandstone which underlies the area.

It seems likely that halite from other lake deposits and salt springs will be found to be red-fluorescing, just as red-fluorescing calcite has been found in recent years to be of wide occurrence.

The specimens from Amboy and Borego Valley, California, are aggregates of anhedral halite crystals with an average diameter of around 5 mm. Some of them are dirty brown in color because of inclusions of clay and organic matter; others are white and translucent. The Idaho samples are efflorescent crusts, about 2 cm. thick, made up of poorly crystallized, translucent halite, and tinged a faint red by fine-grained inclusions of iron oxide.

⁷ Dake, H. C., and DeMent, Jack, *Ultraviolet Light and Its Applications*, p. 129. Chemical Publishing Co., Brooklyn (1941).

⁸ Personal communication from Thomas S. Warren of Los Angeles, California, April 14, 1944. We are indebted to Mr. Warren for a number of specimens from the two California localities.

⁹ Phalen, W. C., *U. S. Geol. Survey, Bull.* **669**, 132 (1919).

¹⁰ Phalen, W. C., *op. cit.*, p. 185.

¹¹ Mansfield, G. R., *U. S. Geol. Survey, Prof. Paper*, **152**, 340 (1927).

WAVELENGTH OF EXCITATION

Two types of mercury vapor lamps were first used in our studies. Spectrograms of the light emitted by these lamps, with their respective filters attached, are shown in Fig. 1.

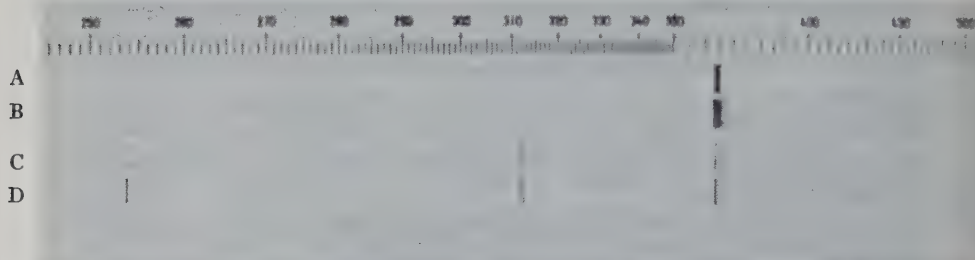


FIG. 1. Spectrograms of light emitted by two types of mercury vapor lamps. Taken with Gaertner medium quartz spectrograph and Eastman I-F plate. A, Inspectolite, 10 secs. B, Same 40 secs. C, Mineralight 20 secs. D, Same, 80 secs. Scale in millimicrons.

Spectra A and B are from a high pressure glass mercury vapor lamp (Hanovia Inspectolite) with a power input of 125 watts. Practically all of the light is emitted in a narrow region around 3660 A. U. Spectra C and D are from a low pressure quartz mercury vapor lamp (Ultra-Violet Products Mineralight) with a power input of 14 watts. According to the manufacturer's catalog, this lamp emits about 90% of its total radiant energy through the 2536 A. U. resonance line of mercury. It was found early in our study that both the natural halite specimens and the synthesized manganiferous salt crystals would not fluoresce under the Inspectolite lamp, so all further work was done with the Mineralight lamp.

The synthetic crystals stop fluorescing as soon as the lamp is turned off, but the natural samples show varying degrees of whitish phosphorescence which is never very strong and is most marked in some of the specimens from Idaho. It is believed that this phosphorescence is due to another, as yet unidentified activator, and not manganese.

SPECTROGRAPHIC ANALYSIS FOR MANGANESE

A few typical pieces of red-fluorescing halite from Idaho and from California were analyzed spectrographically for manganese. Each specimen was first dissolved in water, the insoluble impurities filtered off, and the solution taken to dryness, the activator being water soluble. The crystallized salt was ground thoroughly and duplicate 15 mg. portions

were used to obtain the spectrograms on Eastman III-F plate by means of the Gaertner medium quartz spectrograph.

The amount of manganese was determined from the density of the line at 2798.27 A. U. compared with the densities in spectra of standard samples exposed on the same plate. The standard samples consisted of reagent grade sodium chloride (Mn free) containing graduated amounts of manganous chloride. The analytical results were as follows:

<i>Sample</i>	<i>Wt. % Mn</i>
Salt made from natrolite	0.3
Idaho 1	.00028
Idaho 2	.00025
Idaho 3	.00019
Amboy 1	.00033
Amboy 2	.017
Amboy 3	.0011

The Idaho samples fluoresce more weakly than do the samples from Amboy, California, but, as shall be shown later, the brightness of fluorescence is not determined entirely by the concentration of manganese.

CHEMICAL OBSERVATIONS

When the fluorescing halite specimens were dissolved in water, and the solution filtered and evaporated, the resulting crystals also fluoresced red. This showed that the activator was either soluble in water or, as seems less probable, was of colloidal size. Both the natural and synthetic specimens turned a faint brown and lost their fluorescence when heated for a few hours on a hot plate at around 300°C. When such heated crystals were recrystallized in water, they did not regain their fluorescence but would do so if a few drops of hydrochloric acid were added to the water before recrystallizing. Reagent grade sodium chloride was carried through these tests as a blank. It did not turn brown on heating or show a fluorescence at any stage of the experiment.

These various effects may be accounted for satisfactorily on the basis that bivalent manganese is essential for producing the fluorescence. The development of a brown color and the loss of fluorescence upon heating are due to the bivalent manganese being oxidized to one of the higher oxides of manganese through reaction with atmospheric oxygen. The restoration of fluorescence through the use of hydrochloric acid may be explained by the reducing action that this acid has on the higher manganese oxides which converts manganese back to the bivalent state. Organic compounds, which are known to cause fluorescence in some minerals, seem to be definitely eliminated from consideration by the tests described above.

Iron or cobalt might also show the effects that were observed. Iron was readily eliminated by a trial synthesis that showed that it produces no fluorescence in salt. The result for cobalt was also negative though less decisive. A very faint reddish fluorescence was seen in crystals grown from a cobaltiferous mother liquor, but the "chemically pure" cobaltous chloride that was used in the experiment was later found to contain a small amount of manganese. This illustrates the difficulty caused by impurities that are present in reagents in amounts that are negligible for ordinary chemical purposes but loom large where fluorescence effects are involved. Cobalt was not found in any of the many samples of both natural and synthetic fluorescent halite which were analyzed spectrographically during the course of this study.

Thus all evidence points to small amounts of manganese activating a red fluorescence in sodium chloride, and the story would be complete were it not for a puzzling localization of fluorescence that was noted in both the natural and synthetic specimens.

LOCALIZATION OF FLUORESCENCE

The crystalline aggregates that make up the samples from the three Western localities do not give off a uniformly diffused fluorescence, but rather show small areas, and in some specimens, lateral zones which fluoresce brighter than the rest. This is best seen in the more coarsely crystallized samples that come from the two California localities.

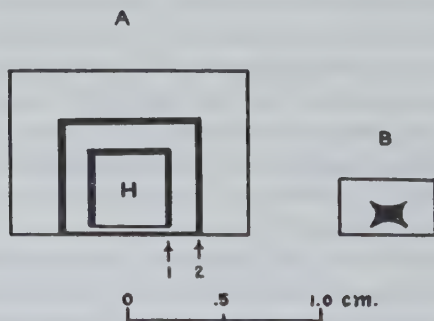


FIG. 2. Localized fluorescence in synthetic manganiferous salt crystals. A. Vertical section of a crystal grown with a cleavage piece of nonfluorescing halite (H) as a seed nucleus. Fluorescent zone 1 deposited during the first day from manganiferous brine. Nonfluorescent portion between 1 and 2 deposited during the next three days. Fluorescent zone 2 deposited upon addition of small amount of lead nitrate to mother liquor. B. Side view of a crystal with typical, hopper-shaped fluorescent core obtained from unseeded manganiferous brine.

In growing salt crystals in the laboratory, it was noted that invariably only the crystals that were deposited during the first day or so from

manganiferous brine fluoresced brightly, and later crops were either only feebly fluorescent or not at all. Moreover, with the crystals of the first crop the fluorescence was restricted to that part of the crystal that formed first, namely, the hopper shaped core shown in Fig. 2 B. When pieces of natural halite selected for their uniform fluorescence were dissolved in water and crystallized, again only the first formed crystals fluoresced, and these had their fluorescence restricted to the core as shown in Fig. 2 B.

The same phenomenon was seen when a cleavage piece of non-fluorescent halite from Detroit, Michigan, was used as a seed (see Fig. 2 A). Only a narrow zone, marked No. 1, nearest the original seed fluoresced brightly and the crystal continued to grow by accretion of nonfluorescent salt. Samples from the two California localities contain many crystals with just such narrow, fluorescent zones.

All laboratory syntheses were carried out with 33.5 ml. portions of a stock solution of reagent grade sodium chloride saturated at room temperature (25°C.). Reagent grade $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was weighed and added to the saturated brine, which was then undersaturated with four drops of water and allowed to evaporate in a 100 ml. pyrex beaker. Amounts of manganese less than a milligram were introduced into the saturated brine by adding the required number of calibrated drops of a manganous chloride solution of known strength. When successive crops of salt were harvested, the mother liquor was decanted into a 50 ml. beaker every two days and undersaturated with three drops of water before further evaporation. The range of initial concentrations of manganese studied was 0.083 to 1,200 mg. Mn per liter.

The deposition of nonfluorescent salt after the first day or so in the various experiments was puzzling because the mother liquor still contained most of the manganese which was initially added. The mother liquor of one preparation was decanted off after it had deposited non-fluorescent salt for several days and the manganese in it was determined gravimetrically as the pyrophosphate. Eighty per cent of the original manganese was present in half the original volume.

Yamamoto,¹² who studied the influence of various metal ions on the growth of alkali salt crystals from water solutions, has shown that over a considerable range of manganese concentration the amount of manganese in the first crop of salt may be represented as an exponential function of the manganese concentration in solution, and in general is only a few per cent of what it would be if manganese and salt were deposited in the ratio prevailing in the mother liquor. Thus there would be an increase in the concentration of dissolved manganese, as the deposi-

¹² Yamamoto, Takemaro, *Sci. Papers Inst. Phys. Chem. Research*, **35**, 228-289 (1939).

tion proceeded and the volume of solution decreased through evaporation.

In preparing thallium-activated, blue-fluorescing potassium chloride from water solutions, Pringsheim¹³ noted that the early crops fluoresced most brightly, but here the explanation was found in the rapid coprecipitation of thallium by potassium chloride. For example, Pringsheim found that by the time 5% of the potassium chloride in a saturated solution had deposited 99% of the thallium originally present had been removed from solution.

The simplest explanation that occurred to us for the localization of fluorescence in our salt crystals was that some unexpected impurity was present in our solutions, that this impurity was also necessary for producing the red fluorescence, and that it was rapidly removed from solution by the first crops of salt just as thallium is by growing crystals of potassium chloride. This explanation proved to be correct, and lead was identified as the second essential activating element.

The presence of traces of lead in all of our natural and synthetic fluorescent salt samples had been established spectrographically early in the study, but the element was not given serious consideration at first for several reasons, (1) its amount was small, (2) it was not known to activate fluorescence in very many compounds, and finally, (3) traces of lead had been encountered in so many rocks and minerals and in practically all chemical reagents during the course of spectrographic work in our laboratory that we had fallen into the habit of accepting traces of lead as commonplace and uninteresting.

The clue that finally pointed to lead as the second essential activating element was found in some spectrograms taken to test the unlikely possibility that, for some reason, growing salt crystals stopped adsorbing manganese after the first couple of days, and that later crystals would not fluoresce because they contained no manganese. Three successive, two-day crops from one manganiferous mother liquor were spectrographically analyzed in duplicate, the first crop being, as usual, the only one that fluoresced.

Figure 3 shows a small portion of duplicate spectra of these three crops in the region of 2800 Å. U., and the three sensitive lines of manganese (2794.82, 2798.27, and 2801.06 Å. U.) are seen to be of same strength in all of the spectra, indicating that the nonfluorescent crystals of crops 2 and 3 contain as much manganese as do the fluorescent crystals of crop 1. Fortunately, the most sensitive line of lead is also located in this spectral region, and lead, which previously had been ignored, forced itself upon our attention. The minute amount of lead

¹³ Pringsheim, Peter, *Rev. Mod. Physics*, **14**, 132-138 (1942).

which had been present in our reagents as a ubiquitous impurity was shown concentrated in the only crop of crystals that fluoresced.

With this clue, a small amount of lead nitrate was purposely added to a manganiferous brine that had been depositing nonfluorescent salt around a seed crystal for several days, and to our delight another

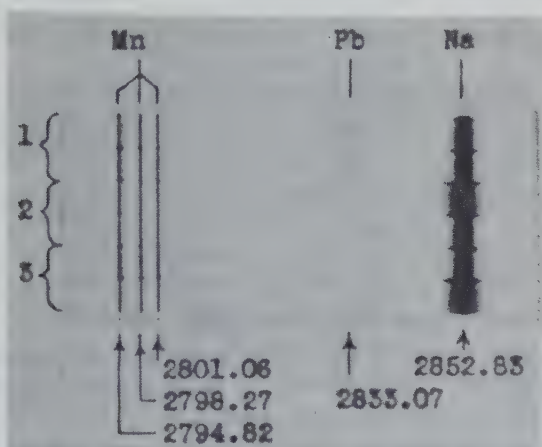


FIG. 3. Spectrographic analysis, in duplicate, of three successive crops of salt from a manganiferous mother liquor. The lead impurity is seen concentrated in the first crop, the only one that fluoresced. Wavelengths in anstrom units.

fluorescent zone formed like the one marked No. 2 in Fig. 2 A. By varying the amount of lead, fluorescent zones of any thickness could be formed around a seed crystal, or a mother liquor could be made at will to deposit crops of fluorescent crystals for any number of days.

Neither manganese nor lead alone will produce a fluorescence or, at most, only a barely detectable fluorescence at high concentrations in the salt. But the two together in amounts of the order of a few thousandths of a per cent will coactivate a vivid red fluorescence.

ADSORPTION OF MANGANESE

Because manganese, unlike lead, is not removed in disproportionate amounts from solution by growing crystals of salt and because reagent-grade sodium chloride is essentially free of manganese, it was possible to determine a lower limit of concentration of manganese below which the first crop of crystals did not fluoresce even when an adequate amount of lead was present in the mother liquor. A series of saturated salt solutions were made up to contain a rather high concentration of lead (1 mg.

Pb per liter) with variable amounts of manganese, and the fluorescence of the first crops was noted. The results are assembled in Table 1.

With the mother liquor containing 0.08 mg. Mn per liter, a barely detectable fluorescence of uncertain hue was produced when the initial lead concentration was raised to 20 mg. Pb per liter, a value probably never attained in nature. This feeble fluorescence is probably due largely

TABLE 1. COMPOSITION OF MOTHER LIQUORS AND FLUORESCENCE OF THEIR FIRST CROPS OF CRYSTALS

Prep. No.	Mg. per liter		Fluorescence
	Pb	Mn	
1	1	400	Bright
2	1	125	Bright
3	1	8	Somewhat weaker
4	1	0.8	Weak
5	1	.08	None
6	20	.08	Barely detectable; color uncertain
7	25	.00	Barely detectable; color uncertain

to lead as a blank preparation (No. 7), also high in lead, produced crystals that fluoresced similarly. Crystals of preparation No. 4 fluoresced more weakly than do the samples from the two California desert localities. The conclusion seems to be indicated that the desert brine at these localities must have contained at least several milligrams manganese per liter and probably even greater amounts, if, as was likely, the lead concentration was smaller than 1 mg. Pb per liter.

Natural bottom waters, both fresh and marine, are known to contain as much as 15 mg. Mn per liter, when they lie stagnant over bottom sediments in which anaerobic decomposition of organic matter is proceeding actively. Concentrations as high as 50 mg. Mn per liter were noted by Robinson¹⁴ in laboratory experiments with submerged soils. However, if fluorescent salt crystals are deposited from a brine of such a chemically reducing nature the brine would have to be low in sulfate; otherwise, hydrogen sulfide may be generated which would precipitate lead sulfide and reduce the concentration of dissolved lead. Manganese may also be precipitated as the sulfide, but the acidity resulting from carbonic acid liberated by decomposing organic matter would tend to keep the element in solution.

The crystals of preparation No. 1, whose mother liquor contained

¹⁴ Robinson, W. O., *Soil Sci.*, **30**, 197-217 (1930).

400 mg. Mn per liter, were found spectrographically to contain 0.008% Mn. For our purpose it may be safely assumed that in the lower ranges the amount in the deposited salt is directly proportional to the concentration in solution, so a mother liquor containing 40 mg. Mn per liter would be expected to yield salt with a manganese content of around 0.0008%, a value well within the range found for natural, fluorescent halite.

COPRECIPITATION OF LEAD

The abstraction of disproportionately large amounts of lead from brines by growing sodium chloride crystals has been demonstrated by Käding,¹⁵ who worked with extremely low concentrations of the order of 3×10^{-6} mg. Pb per liter; and by Yamamoto,¹⁶ who covered the range of 21–561 mg. Pb per liter. In our use of lead nitrate to synthesize fluorescent salt, we made up the manganiferous mother liquors to contain initial concentrations of 0.9–93.0 mg. Pb per liter.

For the concentration range covered in our respective work, both Yamamoto and we found it necessary to use small amounts of either nitric or hydrochloric acid to prevent the lead from precipitating as the chloride. Our early syntheses were carried out with solutions to which no lead had been added, but which nevertheless contained it as an unsuspected impurity, in an amount roughly estimated to be around 0.1 mg. Pb per liter, largely contributed by the reagent-grade sodium chloride. No acid was added to these solutions, but the same rapid removal of lead was observed with them as with the solutions holding larger amounts of lead.

The early removal of most of the dissolved lead by growing salt crystals thus would tend to limit the quantity of fluorescent salt that a given manganiferous brine could produce, and would also cause localization of fluorescence within crystals when the supply of lead is limited.

Although the removal of lead is rapid in the beginning, the rate becomes slower with decreasing concentration. Small amounts persist in solution and appear as spectrographic traces in the later crops of crystals. This probably explains the persistence of a feeble red fluorescence in later crops of crystals from mother liquors containing high concentrations of manganese of the order of 1000–2000 mg. Mn per liter. It is evident that the brightness of fluorescence depends on the amounts of both lead and manganese, and within limits a higher content of one will compensate for a deficiency of the other. Nevertheless, as with manga-

¹⁵ Käding, Hans, *Zeit. physik. Chem.*, **162A**, 174–186 (1932). See also Hahn, Otto, *Applied Radiochemistry*, pp. 102–113, Cornell Univ. Press (1936).

¹⁶ Yamamoto, Takemaro, *op. cit.*, pp. 260–262.

nese, there appears to be a limiting value of lead below which a bright fluorescence is not produced no matter how great an amount of manganese is present in the crystal. Fluorescent zones like those shown in Fig. 2 A show fairly sharp outer boundaries, instead of gradual transition from bright to dim fluorescence, which also suggests the reality of such a limiting concentration of lead. The lead content of the natural, brightly fluorescent halite specimens has not been accurately determined, but a rough estimate based on the intensity of the 2833.07 Å. U. line in the spectrograms would be 0.001–.01% Pb.

MISCELLANEOUS OBSERVATIONS

As barium, univalent thallium, and bismuth are somewhat similar in their chemical behavior to lead, small amounts of their salts were tried as substitutes for lead in coactivating the red fluorescence with manganese, but the results were negative. Stannous chloride with manganese also gave a negative result. As far as can be told from our brief survey, the manganese-lead pair is unique in producing the red fluorescence; and the relationship may find use as a basis for a qualitative test for small amounts of lead.

A manganiferous, saturated salt solution undergoing evaporation is extremely sensitive to lead, and will betray even very small amounts of it by depositing fluorescent salt. This was illustrated in one preparation in which an acid-free mother-liquor, which had become depleted of its lead, "crept" up the side of the beaker and coated the outside with a thin layer of salt. Under the ultraviolet lamp the Pyrex brand on the beaker fluoresced bright red against a background of nonfluorescent salt. By itself, the brand does not fluoresce at all. Subsequently, it was learned that a flux of lead borate is used to fix the brand on the glass surface. The creeping salt solution had extracted enough lead from the letters to cause the salt deposited over them to fluoresce brightly.

The aim in our study has been to work out the gross, qualitative aspects of this interesting coactivation of a red fluorescence in sodium chloride by manganese and lead, and it is evident that the system deserves a more thorough and precise study.

ACKNOWLEDGMENTS

We are indebted to Mr. Thomas S. Warren of Los Angeles, California, for samples of red-fluorescing halite from the two California localities. Drs. W. T. Schaller, C. S. Ross, Michael Fleischer, and Mr. W. G. Schlecht of the Geological Survey have critically read the manuscript of the paper and made many helpful suggestions. We express our hearty thanks to Mr. Warren and our colleagues for their generous help.

NOTES ON THE STRUCTURE OF DELAFOSSITE

A. PABST,
University of California, Berkeley, California.

ABSTRACT

From a consideration of interionic radii and coordination it is shown that delafossite, CuFeO_2 , is probably to be considered cuprous metaferriite. That is, the copper is present as cuprous ions and the iron as ferric ions.

Eight years ago I reported to the society¹ on a comparison of spacing measurements derived from powder patterns of delafossite with spacings calculated for the structure of artificial CuFeO_2 which had been briefly described by Soller and Thompson. It was concluded that delafossite probably has the same structure as Soller and Thompson's artificial material.²

The density calculated from this structure, 5.52 (using the same value of Avogadro's number used by Siegbahn, since it is assumed that Soller and Thompson used Siegbahn wave-lengths), greatly exceeds the value 5.07, then current in the literature, or the highest values I had then been able to obtain from the material used. A few years ago the late Dr. Berman reported to me that the value 5.41 had been obtained on an 8 mg. crystalline sample and this value is now incorporated in the seventh edition of Dana's *System of Mineralogy* and credited to Frondel.

Table 1 shows the spacing measurements and intensity observations on powder patterns of delafossite from various sources compared with theoretical spacings corresponding to the lattice of Soller and Thompson. The discrepancies between the several sets of spacings, especially between the records taken from other publications and those obtained during this work, give an indication of the sort of departures that are often met in x-ray identification work. These are probably not due to variations in the delafossite. The smaller differences are near the limits of accuracy of measurement, or may be due to differences in the manner of handling the data, but the absence of any line near 1.253 and the presence of a line at 1.080 reported by Harcourt are somewhat disturbing. It seems unjustified to attribute the 1.080 line to contamination when there is no suggestion of other such lines in the range of the larger spacings where they would be more likely. It seems probable that Harcourt's report on a delafossite pattern leaves something to be desired in the way of careful observation and reporting.

¹ Crystal structure and density of delafossite (abstract only), *Am. Mineral.*, **23**, 175-176 (1938).

² It had earlier been assumed by Ramdohr (*Zentralbl. f. Mineral.*, **A**, 289-303 (1937)) that such is the case.

TABLE 1. INTERPLANAR SPACINGS OF DELAFOSSITE

		Calcu- ated spacings†	Observed spacings and intensities									
			Bisbee Pabst#		Kimberley Pabst#		Waldo*		Bisbee Harcourt**			
<i>hkl</i>	<i>h,k,l_r</i>	<i>d</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>		
0006	222	2.85	2.87	.45	2.85	.40	2.84	m	2.84	1.0		
0112	110	2.49	2.52	1.20	2.51	1.15	2.49	s	2.51	5.0		
1014	211	2.235	2.246	.50	2.230	.45	2.22	m	2.23	1.0		
0118	332	1.656	1.670	.45	1.666	.40	1.650	m	1.66	1.0		
1120	101	1.512	1.516	.35	1.511	.35	1.507	m	1.515	1.0		
101.10	433	1.432	1.436	.35	1.436	.35	1.428	m	1.435	0.5		
000.12	444	1.424										
1126	321	1.337	1.349	.25	1.339	.25	1.332	m	1.340	1.0		
011.11	443	1.337										
2022	200	1.296	1.293	.15	1.295	.15	1.289	w	1.295	0.5		
0224	220	1.253	1.251	.10	1.253	.05	1.247	w	1.080	0.2		
2028	422	1.117	1.116	.10	1.118	.10	1.113	vw				
022.10	442	1.039	1.040	.20	1.039	.15	1.036	w				
112.12	543	1.037										
1232	211	.985	.983		.984		.988	vw				
2134	310	.966	—		.966		.962	ew				
							.949	ew				
1238	431	.899	.898		.896		.898	vw				
3030	211	.873	—		.876		—	—				
					.860		.853	vw				
					.830		—					
					—		.813	ew				
					.807		.804	vw				

† For a cell of dimensions $a_r = 5.96$, $a = 29^\circ 26'$; $a_h = 3.03$, $c_h = 17.09$.

Mo radiation. Intensities recorded in heights of peaks on photometer curves in centimeters. Diffraction patterns obtained through the courtesy of Mr. W. H. Dore, Division of Plant Nutrition, University of California.

* A. W. Waldo, Identification of the copper ore minerals by means of x-ray diffraction patterns: *Am. Mineral.*, **20**, 575-597 (1935). Radiation not indicated, s—strong, m—medium, w—weak, vw—very weak, ew—exceptionally weak.

** G. A. Harcourt, Tables for the identification of ore minerals by x-ray powder patterns: *Am. Mineral.*, **27**, 63-113 (1942). Radiation not indicated.

The technique of x-ray identification of crystalline materials, after many years of slow growth has been making more rapid progress in recent years. Unfortunately such failings as that just indicated are likely to be a hindrance. More crystallographic indexing of films and more checks against the literature of crystal structure wherever possible by those who use and especially by those who publish powder data for identification purposes seem to be called for. There are, of course, many cases where such indexing or checking is not feasible, but it has often

been omitted for no better reason than that the authors found it too tedious.

Delafossite was first reported from America by Professor Rogers when he described crystals from Bisbee in 1913.³ At that time Professor Rogers considered the chemical constitution of the mineral and tried to determine the valence of the copper and iron. After several chemical experiments which were not fully decisive it was concluded that "delafossite is probably cuprous metaferrite, $\text{Cu}'\text{Fe}'''\text{O}_2$."

Various methods not available thirty years ago might now be used to discriminate between $\text{Cu}'\text{Fe}''\text{O}_2$ and $\text{Cu}'\text{Fe}'''\text{O}_2$. The method most appropriate to the present case depends on determination of interionic distances in the crystal lattice.

TABLE 2. SUMMARY OF INTENSITY CALCULATIONS FOR DELAFOSSITE WITH Cu IN 0, 0, 0 Fe IN $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ AND O IN u , u , u AND \bar{u} , \bar{u} , \bar{u} , AND INTENSITY OBSERVATIONS WITH Mo RADIATION

		Calculated							Observed*	
		$u1/9^\#$		1/9		1/10	0.23	7/18	Bis- bee	Kim- berley
hkl	$h_r k_r l_r$		Δ		Δ					
0003	111	9		10		2	4	51	—	—
0006	222	161	13	174	32	142	150	174	.45	.40
10 $\bar{1}$ 1	100	43		36		40	5	10	—	—
01 $\bar{1}$ 2	110	510	19	529	29	558	264	529	1.20	1.15
10 $\bar{1}$ 4	211	187	9	196	17	213	505	196	.50	.45
01 $\bar{1}$ 5	221	8		7		9	12	24	—	—
0009	333	7		7		5	6	2	—	—
10 $\bar{1}$ 7	322	2		2		0	3	0	—	—
01 $\bar{1}$ 8	332	192	1	193	33	160	176	193	.45	.40
			$\Sigma \Delta 42$		$\Sigma \Delta 111$					
1120	10 $\bar{1}$			156		156	156	156	.35	.35
1123	210			1		0	0		—	—
10 $\bar{1}$ ·10	433			116	138	127	74	103	.35	.35
000·12	444			22		32	29		.25	.25
1126	321			108	109	92	96	97		
01 $\bar{1}$ ·11	443			1		4	1		—	—
0221	11 $\bar{1}$			2		4	1		.15	.15
2022	200			58		65	45		.10	.05
0224	220			36		38	75			

Calculated with ionic f_0 values. All other intensities calculated with atomic f_0 values. See text.

* Observed intensities measured by heights of peaks on photometric curve in centimeters.

³ Delafossite, a cuprous metaferrite from Bisbee, Arizona: *Am. Jour. Sci.*, **35**, 290–294 (1913).

Before proceeding with this it seemed best to check the observed intensities of delafossite powder patterns against intensities calculated from the structure. Table 2 gives all pertinent data. It is seen that the observed intensities of lines on two patterns agree well with the intensities corresponding to the structure given by Soller and Thompson⁴ with one CuFeO_2 in a rhombohedral cell ($a_r = 5.96$, $\alpha = 29^\circ 26'$; $a_h = 3.03$, $c_h = 17.09$) Cu in 0, 0, 0 Fe in $1/2, 1/2, 1/2$ and O in $1/9, 1/9, 1/9$ and $8/9, 8/9, 8/9$. It is to be noted, however, that the lines observed all have $h+k+l=2n$. The intensities of these lines would be the same if any parameters are altered by $1/2, 1/2, 1/2$. Hence there is no difference in the intensity of these lines for O in $1/9$ ($8/9$) etc. i.e., $2/18$ ($16/18$) etc., or in $11/18$ ($7/18$) etc. The intensities of lines for which $h+k+l \neq 2n$ are affected by such a parameter change, but no such lines are observed in powder patterns.

Most of the intensity calculations recorded in Table 2 have been made with f_0 values for the neutral atoms as given in the *International Tables for the Determination of Crystal Structures*, vol. II, pp. 571 and 572. It may seem that it would have been better to use the scattering factors for the appropriate ions, especially since one of the objects of this work is to check on the valence state of the metals in the structure. Unfortunately tables are lacking for copper or iron ionic scattering factors. The difference in calculated intensities would be slight except for the first line or two, since the scattering power of O and O^{-2} , which differ by 25% at zero scattering angle, differ by only 4.7% at the angle for 222 of delafossite and even less for other lines. For iron and copper the proportional difference in the scattering factors would be much less. Nevertheless, a calculation with improvised ionic scattering factors for Cu^{+1} and Fe^{+3} and the accepted values for O^{-2} has been made for the first ten lines to show that no discrimination as to valence state of the ions is possible on this basis. Comparing the calculated intensities in the first three columns of Table 2 one can conclude that the effect on the intensities of diffracted beams due to change of internuclear distances attending valence change outweighs the effect due to change in scattering power.

Figure 1 shows the variation in intensities of the first ten possible powder lines with variation in the oxygen parameter from 0 to $\frac{1}{2}$. It is seen that Soller and Thompson's choice of parameter is well justified, if we take into account that reducing it below $1/9$ is excluded by atomic radii, but that $7/18$ gives equally satisfactory agreement of observed and calculated intensities. Our diagram shows also that observation of 100

⁴ Soller, Walter, and Thompson, A. J., The crystal structure of cuprous ferrite: *Phys. Rev.*, **47**, 644 (1935).

and/or 111 or, best of all, a pattern on which the odd orders of hhh could be compared would make possible a choice.

Accepting for the moment the oxygen parameter of $1/9$ we may draw a picture of the structure and also determine interatomic distances and coordinations. Figure 2 shows such a structure in clinographic projection and 2a shows a section through it on a symmetry plane.

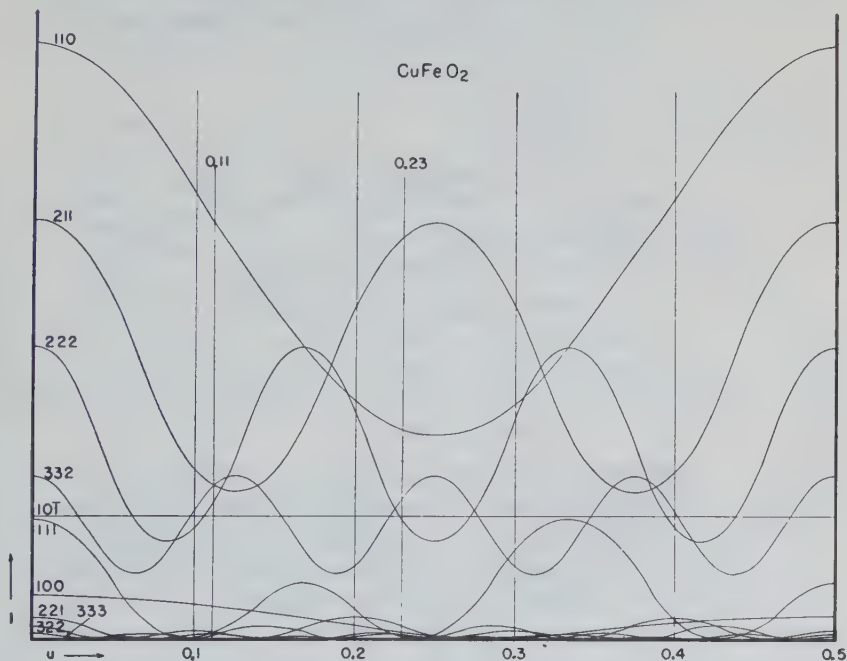


FIG. 1. Variation of intensities of the first ten possible powder lines of delafossite with variation of the oxygen parameter from 0 to $\frac{1}{2}$.

In Fig. 2a the radii of the circles representing the ions are made proportional to the ionic radii of Cu (0.96), Fe (0.67), and O (1.32) given by Evans.⁵ It is seen that there is overlap of O on adjoining O and on Cu in this case.

If O is given the parameter $7/18$, which is in equally good agreement with observed intensities, the configuration shown in the section in Fig. 2b results. In this case the overlaps are similar. The coordination, however, is quite different in the two cases. With the parameter $1/9$ Cu has a twofold coordination of O about it and Fe a sixfold coordination of O about it. If the oxygen is at $7/18$ these coordinations are interchanged.

⁵ Evans, R. C., *Crystal Chemistry*, Cambridge (1939), p. 171.

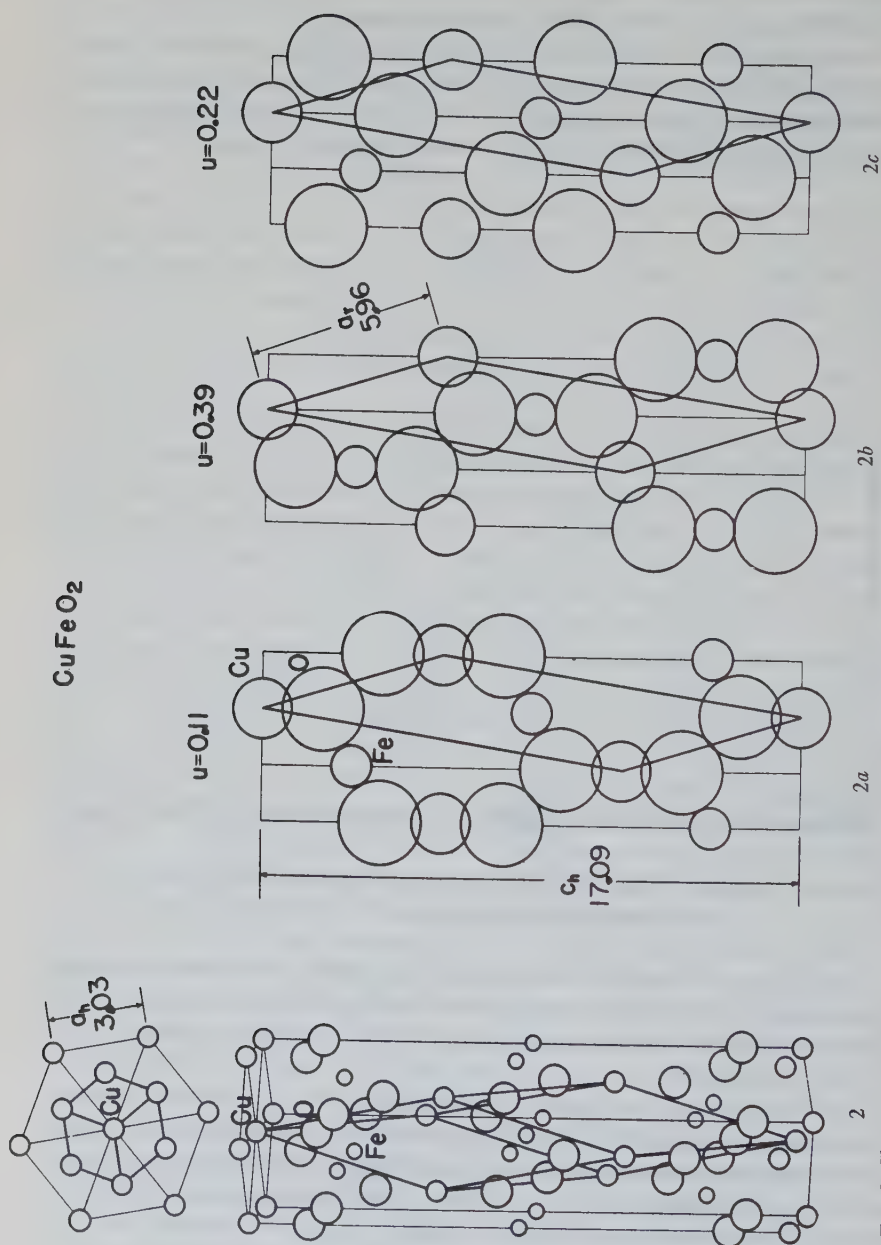


FIG. 2. Clinographic projection of delafossite structure with oxygen parameter $1/9$ or 0.11 . Figs. 2a, 2b and 2c. 1210 sections through delafossite structures with various oxygen parameters.

It is possible to find an oxygen position in which the distance from oxygen to both Fe and Cu is fully that required by ionic radii. If O is given the parameter 0.23, as in Fig. 2c, both Cu and Fe have sixfold coordination and there are no overlaps. If this parameter is decreased the O-O distance and the Fe-O distance are decreased, whereas the Cu-O distance is increased. Since parameters in this range are, however, excluded by intensity observations they will not be further considered no matter how reasonable the corresponding structures.

TABLE 3. COMPOUNDS HAVING THE CRYSTAL STRUCTURE TYPE $F 5_1$

Formula	$\angle \alpha$	a_r	u	Strukturbericht
NaHF ₂	40° 2'	5.05	0.41	Vol. I
CaCN ₂	43 50	5.11	0.37	Vol. I
NaN ₃	38 43	5.48	0.42	Vol. I
CsICl ₂ [#]	70 42	5.46	0.31	Vol. I
CuFeO ₂	29 26	5.96	0.11	Vol. III
NaFeO ₂	31 20	5.59	0.22	Vol. III

[#] In Strukturbericht I, CsICl₂ is referred to "Idealfall II" under type $F 5_1$. Wyckoff, on the other hand, makes this the type, his d of the RX_3 compounds, and refers the first three of this list to it.

In Volume III of the Strukturbericht CuFeO₂ is referred to type $F 5_1$ for which NaHF₂ was taken as the example in volume I. Table 3 lists the structures which have been referred to this type. It is seen that NaFeO₂ is the only one whose lattice dimensions approach closely those of CuFeO₂. The structure of NaFeO₂ was determined by Goldsztaub.⁶ He assigned Na to 0, 0, 0; Fe to 1/2, 1/2, 1/2 and selected 2/9 for the value of the oxygen parameter. This is close to the value just considered for CuFeO₂ and discarded because of intensities, and gives both the Na and the Fe a sixfold coordination.

TABLE 4A. INTERIONIC DISTANCES AND COORDINATION IN DELAFOSSITE

	O in 1/9, 1/9, 1/9 and 8/9, 8/9, 8/9		O in 7/18, 7/18, 7/18 and 11/18, 11/18, 11/18	
	Distance	Coordination	Distance	Coordination
O-O	2.583	3	2.583	3
Fe-O	1.991	6	1.899	2
Cu-O	1.899	2	1.991	6

⁶ Goldsztaub, M. S., Etude de quelques derives de l'oxyde ferrique (FeO · OH, FeO₂Na, FeOCl); determination de leurs structures: *Bull. soc. fran. min.*, **58**, 6-76 (1935).

Referring to the structure of delafossite, interionic distances and coordinations for $u=1/9$ and $u=7/18$ are tabulated in Table 4A. A choice between these two parameters cannot be made from the x -ray data available to me and I am unable to say just how Soller and Thompson made their choice, or indeed, whether they considered $7/18$ as a possibility. A comparison with known metal-oxygen distances and coordination num-

TABLE 4B. INTERIONIC DISTANCES IN SIMPLE OXIDES OF Cu AND Fe

Material	Interionic Distance	Coordination	Reference
Cuprite Cu_2O	1.843 $\text{Cu}'\text{-O}$	2	Niggli, <i>Zeits. Krist.</i> , 57 , 253 (1922).
Tenorite CuO	1.95 $\text{Cu}''\text{-O}$	4	Tunnell, Posnjak and Ksanda, <i>Zeits. Krist.</i> , 90 , 120 (1935).
Wustite FeO	2.14 $\text{Fe}''\text{-O}$	6	Wyckoff and Crittenden, <i>Zeits. Krist.</i> , 63 , 144 (1926).
Hematite Fe_2O_3	2.06 1.91 $\text{Fe}'''\text{-O}$	$\left. \begin{matrix} 3 \\ 3 \end{matrix} \right\} 6$	Pauling and Hendricks, <i>J.A.C.S.</i> , 47 , 781 (1925)

bers in the simple oxides of iron and copper is some help in this connection. The pertinent data with references are given in Table 4B. From this it may be seen that with the parameter $1/9$ we may interpret delafossite as being cuprous metaferrite, $\text{Cu}'\text{Fe}'''\text{O}_2$, as surmised by Rogers, and that both copper and iron will then have the coordination and nearly the same metal-oxygen distances which have been found in the corresponding simple oxides. If we choose the parameter $7/18$ and/or consider delafossite to be $\text{Cu}''\text{Fe}'''\text{O}_2$ there is no way of obtaining such an agreement. Pending the availability of better x -ray data we may accept Soller and Thompson's choice of oxygen parameter and conclude that delafossite is indeed cuprous metaferrite as supposed by Rogers.

GNOMONIC AND LINEAR HEPTAXIAL TWO-CIRCLE CALCULATION

A. L. PARSONS, *Royal Ontario Museum of Geology and Mineralogy, Toronto 5, Ontario.*

ABSTRACT

Referring an hexagonal crystal to three sets of orthorhombic axes and taking $\phi_{(1-3)}$ and $\phi'_{(1-3)(-90^\circ-\phi)}$ alternatively, gnomonic calculation yields the following:

$$\cos \phi_{1-3} \text{ (or } \phi'_{1-3}) \cdot \tan \rho = \frac{k}{l} \cdot \frac{c}{a} : \frac{(h+2k)c}{l\sqrt{3a}} : \frac{(h+k)c}{la} : \frac{(2h+k)c}{l\sqrt{3a}} : \frac{h}{l} \cdot \frac{c}{a} : \frac{(h-k)c}{l\sqrt{3a}}.$$

Linear calculation yields the following:

$$\tan (90^\circ - \rho) / \cos \phi'_{(1-3)} \text{ (or } \phi_{1-3}) = \frac{l}{k} \cdot \frac{a}{c} : \frac{l}{h+2k} \cdot \frac{\sqrt{3a}}{c} : \frac{l}{h+k} \cdot \frac{a}{c} : \frac{l}{2h+k} \cdot \frac{\sqrt{3a}}{c} : \frac{l}{h} \cdot \frac{a}{c} : \frac{l}{h-k} \cdot \frac{\sqrt{3a}}{c}.$$

The linear constants are a/c and $\sqrt{3a}/c$ and the reciprocal gnomonic polar constants are c/a and $c/\sqrt{3a}$, which, as they may be interchangeable, might be indicated as p_0 and π_0 . The gnomonic polar representation of the facts shown in the linear projection of a face (hkl) is a circle with $\tan \rho$ as diameter, which is used for the graphical determination of the polar constants. The linear projection is shown to be well adapted for use in two-circle calculation.

The calculation of the reciprocal (polar) constants depends on two sets of triangles (not polar) which are homopolar, with one common angle, and with the sides adjacent to this angle having reciprocal tangents.

Five pairs of gnomonic constants are readily derived: two of which are definitely polar and refer to triaxial systems; two others are polar in the sense that they locate the projection point by co-ordinates in three and six directions respectively, and refer to tetraaxial and heptaxial systems and because of the greater number of horizontal axes involved, must be fractions of the reciprocal polar units; the fifth pair are definitely auxiliary units.

Two-circle equations for the calculation of axial ratios and indices in the hexagonal system have been of two kinds; first a simple calculation dealing only with indices and axial ratios which unfortunately has attracted little attention, secondly equations involving various polar constants. In a former paper, the writer (Parsons 1937) attempted, rather unsuccessfully, to harmonize three pairs of polar constants, and in the last paragraph gave the simple equations which have led up to this paper. Later he found that Ford (1922) had given in graphical form the same information, and that Lewis (1899) had used the same principle in connection with the first order unit pyramid. For the writer, the discarding of all polar constants, except c/a and $c/\sqrt{3a}$, from the calculation, the establishment of a simple correlation of the linear and gnomonic constants, and the derivation of the curves involved in the various polar con-

stants, has cleared up the tremendous confusion that has surrounded this system for the past sixty years.

The two-circle calculation of hexagonal constants is best accomplished by referring the crystal to three sets of orthorhombic axes with axial ratios $\sqrt{3}a:a:c$, but before entering upon the hexagonal calculation, it will be well to see what facts may be deduced from the measurement and projection of an orthorhombic crystal as well as the angles that can be determined by trigonometric calculation so that a proper selection of equations may be made for an abridged calculation of crystallographic constants.

In doing this, the writer is accepting the two-circle equations of W. H. Miller (1839, p. 83) for the orthorhombic system, which apply to the linear projection, and is making the changes that are necessary for the gnomonic projection. He is also accepting the Miller and Miller-Bravais indices, and the Miller conventions for form symbols, face symbols, zone axis symbols, and zone (circle) symbols. He would also express his admiration for the Miller precision two-circle goniometer constructed in 1874 (Lewis 1899, p. 601), which was in perfect condition in 1928 at the University of Cambridge.

The Miller (1839, p. 83) equations are as follows:

$$\begin{array}{ll} \tan \phi = ka/hb & \phi = (hko) \wedge (100) = 90^\circ - \phi' \\ \tan \frac{1}{2}L = la/hc \cdot \cos \phi & \frac{1}{2}L = [001] \wedge [hkl] = 90^\circ - \rho \end{array}$$

In the form given, Miller's (1839, p. 79) complete two-circle calculation of the orthorhombic is perfect arithmetically, but obscure graphically. Substituting $\tan 90^\circ - PX$, etc. for $\cot PX$, etc., the equations are identical with those used in the linear calculation in this paper. Substituting $1/\tan PX$, etc., for $\cot PX$, etc., the equations, when inverted, are identical with those used for the gnomonic calculation. Miller's equations have been used by nearly all crystallographers in the past century, sometimes in a mutilated condition. They have never been surpassed; when changed, it has always been for the worse.

CONVENTIONS IN NOTATION

Following Miller's practice, the form symbol is given as $\{hk\bar{l}\}$, the face symbol as $(hk\bar{l})$; the zone axis as $[uvw+vw]$, and the zone circle symbol as $[hk\bar{l}, h0\bar{h}0]$. Miller used $[uvw+vw]$ interchangeably for the zone axis and the zone circle except in one paragraph (p. 48) but commonly used the zone symbol as given above for the zone circle only. This usage enables one to use six types of angles without ambiguity, as follows: $(010) \wedge (110)$, the well known interfacial angle, $[001] \wedge (001)$ or $[001] \wedge (hkl)$ giving ρ_0 or ρ , $(001) \wedge [hkl, 100]$, not used in this paper, $[001]$

TABLE 1. ANGLES FOUND IN TWO-CIRCLE MEASUREMENT OF A CRYSTAL FOR THE FACE (511) ORTHORHOMBIC, (2131) HEXAGONAL

Orthorhombic	Hexagonal
$\alpha = b \wedge c = [001] \wedge [010] = 90^\circ$	$[0001] \wedge [10\bar{1}0]$
$\beta = a \wedge c = [100] \wedge [001] = 90^\circ$	$[12\bar{1}0] \wedge [0001]$
$\gamma = a \wedge b = [100] \wedge [010] = 90^\circ$	$[12\bar{1}0] \wedge [10\bar{1}0]$
$\lambda = (001) \wedge (010) = 90^\circ$	$(0001) \wedge (12\bar{1}0)$
$\mu = (001) \wedge (100) = 90^\circ$	$(0001) \wedge (10\bar{1}0)$
$\nu = (010) \wedge (100) = 90^\circ$	$(12\bar{1}0) \wedge (10\bar{1}0)$
$\rho_0 = [001] \wedge [001] = 0^\circ$	$[0001] \wedge [0001]$
$\rho = [001] \wedge [511] =$	$[0001] \wedge [21\bar{3}1]$
$\rho' = [001] \wedge [511] = 90^\circ - \rho$	$[0001] \wedge [21\bar{3}1]$
$\phi_0 =$	
$\phi = (510) \wedge (010)$	$(21\bar{3}0) \wedge (12\bar{1}0)$
$\phi' = (510) \wedge (100)$	$(21\bar{3}0) \wedge (10\bar{1}0)$
$\eta_0 = [001] \wedge [001, 100] = 0^\circ$	$[0001] \wedge [0001, 10\bar{1}0]$
$\xi_0 = [001] \wedge [001, 010] = 0^\circ$	$[0001] \wedge [0001, 12\bar{1}0]$
$\eta_0' = [001] \wedge [010] = 90^\circ$	$[0001] \wedge [12\bar{1}0]$
$\xi_0' = [001] \wedge [100] = 90^\circ$	$[0001] \wedge [10\bar{1}0]$

To find in the gnomonic projection

$$\begin{aligned}
 \eta &= [001, 100] \wedge [511, 100] & [10\bar{1}0, 0001] \wedge [21\bar{3}1, 10\bar{1}0] \\
 \xi &= [001, 010] \wedge [511, 010] & [12\bar{1}0, 0001] \wedge [21\bar{3}1, 12\bar{1}0] \\
 a, b, c, h, k, l & & \sqrt{3}a, a, c, h, k, i, 2h+k, h+2k, h-k, l
 \end{aligned}$$

And in the linear projection

$$\begin{aligned}
 \eta' &= [001, 100] \wedge [011] = 90^\circ - \eta & [10\bar{1}0, 0001] \wedge [12\bar{1}2] \\
 \xi' &= [001, 010] \wedge [501] = 90^\circ - \xi & [12\bar{1}0, 0001] \wedge [50\bar{5}1]
 \end{aligned}$$

The calculation of these angles follows:

$$\begin{aligned}
 \cos \phi \cdot \tan \rho &= \tan \eta = k/l \cdot c/a \quad (\text{IV and III}) \\
 \cos \phi' \cdot \tan \rho &= \tan \xi = h/l \cdot c/\sqrt{3}a \quad (\text{IV}), = (2h+k)/l \cdot c/\sqrt{3}a \quad (\text{III}) \\
 \tan \rho'/\cos \phi &= \tan \eta' = l/k \cdot a/c \quad (\text{IV and III}) \\
 \tan \rho'/\cos \phi' &= \tan \xi' = l/h \cdot \sqrt{3}a/c \quad (\text{IV}) = l/(2h+k) \cdot \sqrt{3}a/c \quad (\text{III})
 \end{aligned}$$

AXIAL RELATIONS

Before going into the graphical and mathematical solution of an hexagonal problem, it will be well to consider the axial relations and intercepts of a plane on the hexagonal axes. It has been customary to refer an hexagonal crystal to three horizontal axes (a_1, a_2, a_3) of unit length and a vertical axis (c) which is greater or less than unity, and the recorded ratios are $a:c$. It has, however, been recognized that there is a second set of horizontal axes, at right angles to the a axes, having a length of $\sqrt{3}a$, which could be used if results obtained from the first set

proved unsatisfactory. This seems to indicate that the complete solution of an hexagonal problem demands that the relationship of six horizontal axes to the vertical axis should be ascertained.

In x -ray analysis of hexagonal crystals, it is customary to look upon the hexagonal cells as being made up of three unit cells, each an orthorhombic prism with angles of 60° and 120° .

The results of measurement of an hexagonal crystal when plotted in a gnomonic projection indicate three units with axes $\sqrt{3}a:a:c$. In this way we get six horizontal axes, three pairs of rectangular axes, which yield the simplest polar equation of the plane (hkl) for each of the triaxial units involved.

CONSTANTS IN THE LINEAR PROJECTION

In the linear projection (Fig. 2), in order to have a common centre for the three orthorhombic units, they are shown as interpenetrating, and the height of the vertical axis is indicated by a circle with radius equal to

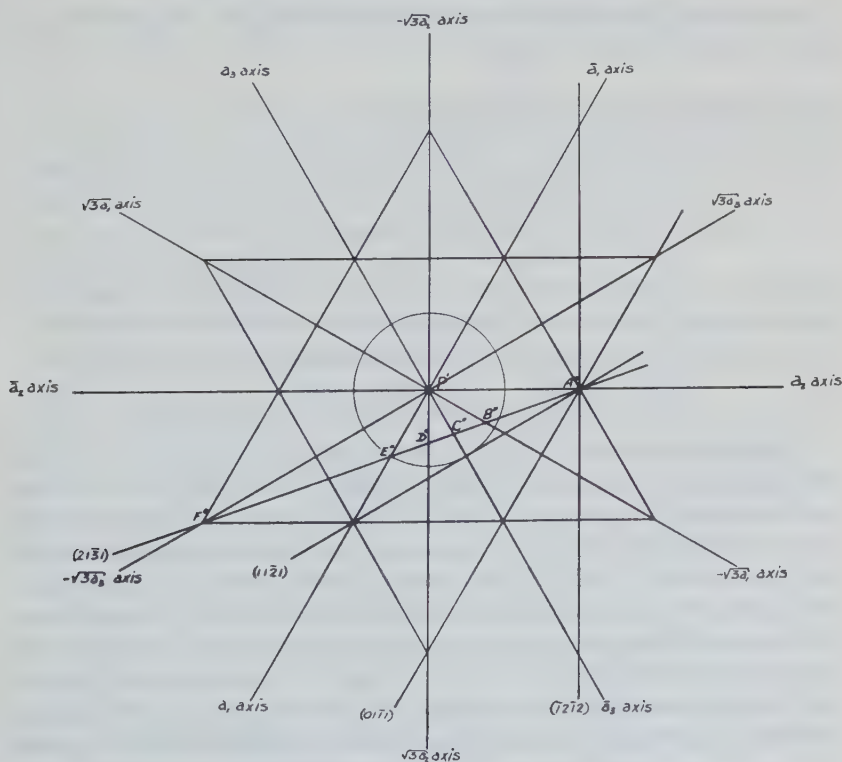


FIG. 2

c (beryl). Of the four faces shown, we will for the present confine our attention to the general case $(21\bar{3}1)$, which cuts the a_2 axis at unity. Careful measurement will show that:

$$\begin{aligned} \frac{P'A''}{c} : \frac{P'B''}{c} : \frac{P'C''}{r} : \frac{P'D''}{c} : \frac{P'E''}{c} : \frac{P'F''}{c} \\ = \frac{l}{1} \cdot \frac{a}{c} : \frac{l}{4} \cdot \frac{\sqrt{3}a}{c} : \frac{l}{3} \cdot \frac{a}{c} : \frac{l}{5} \cdot \frac{\sqrt{3}a}{c} : \frac{l}{2} \cdot \frac{a}{c} : \frac{l}{1} \cdot \frac{\sqrt{3}a}{c} \\ = \frac{l}{k} \cdot \frac{a}{c} : \frac{l}{h+2k} \cdot \frac{\sqrt{3}a}{c} : \frac{l}{h+k} \cdot \frac{a}{c} : \frac{l}{2h+k} \cdot \frac{\sqrt{3}a}{c} : \frac{l}{h} \cdot \frac{a}{c} : \frac{l}{h-k} \cdot \frac{\sqrt{3}a}{c} \end{aligned}$$

which are the abscissae cut off on six axes by the trace of the plane $(21\bar{3}1)$ in the linear projection with the origin *above* the plane of projection and with $r_0 = c$. The linear projection of the same face is shown in Fig. 3 with the origin *below* the plane of projection and with $r_0 = 1$. The ratios shown above are the tangents of interaxial angles (zonal axes).

CONSTANTS IN THE GNOMONIC PROJECTION

If we invert the terms of the equations under linear constants so as to have reciprocal values, we get

$$\begin{aligned} \frac{c}{P'A''} : \frac{c}{P'B''} : \frac{c}{P'C''} : \frac{c}{P'D''} : \frac{c}{P'E''} : \frac{c}{P'F''} \\ = \frac{k}{l} \cdot \frac{c}{a} : \frac{h+2k}{l} \cdot \frac{c}{\sqrt{3}a} : \frac{h+k}{l} \cdot \frac{c}{a} : \frac{2h+k}{l} \cdot \frac{c}{\sqrt{3}a} : \frac{h}{l} \cdot \frac{c}{a} : \frac{h-k}{l} \cdot \frac{c}{\sqrt{3}a} \\ = \frac{PA}{r_0} : \frac{PB}{r_0} : \frac{PC}{r_0} : \frac{PD}{r_0} : \frac{PE}{r_0} : \frac{PF}{r_0} \quad (\text{Fig. 3}) \end{aligned}$$

which are the indices with the axial ratios, and the abscissae, respectively, on the axes of the gnomonic projection when a circle is described with $\tan \rho$ as the diameter. They are also the tangents of interzonal angles.

LINEAR ZONAL AXES AND GNOMONIC ZONE LINES

The line joining c and A'' (Fig. 2) is common to $(21\bar{3}1)$, $(11\bar{2}1)$, $(01\bar{1}1)$, and $(\bar{1}2\bar{1}2)$ and is the axis $[\bar{1}2\bar{1}2]$ of the zone $[\bar{1}2\bar{1}2, 10\bar{1}0]$ in which these four faces lie. In like manner cB'' , cC'' , cD'' , cE'' , and cF'' are zone axes which are perpendicular to the planes which intersect in the normal to the plane $(21\bar{3}1)$ (Fig. 3). The traces of these planes in the gnomonic projection are the familiar zone lines in the projection. The angle between one of these zonal planes and r_0 on the a axes is known as η , and to distinguish the particular axis is indicated in this paper as η_1 , η_2 , and η_3 . The corresponding angle on the $\sqrt{3}a$ axes is known as ξ , with similar indication of the axis involved. The angles subtended between the zonal axes and the perpendicular in the linear projection are $90^\circ - \eta$, and

$90^\circ - \xi$, respectively. These zone axes are best indicated in terms of a possible face as follows: $cA''[1\bar{2}12]$, $cB''[02\bar{2}1]$, $cC''[33\bar{6}2]$, $cD''[50\bar{5}2]$, $cE''[2\bar{1}11]$, and $cF''[1\bar{1}02]$. In the transfer of the linear projection of (2131) (Fig. 2) to the gnomonic projection (Fig. 3) there is a reversal of the sign for l/h , l/k , and $l/h+k$.

HEXAGONAL INDICES

In the hexagonal system, it is customary to use four indices, h , k , i , and l , with three of these referring to horizontal units and one to the vertical unit. Of the horizontal values, one (i) equals the sum of the other two (h and k) but with opposite sign (\pm). Of the twenty-four ways in which these letters may be combined, four at least are given in standard works on mineralogy and crystallography. In a previous paper, the writer used the order given by Williams (1901). In this paper the usage of Dana is followed, as indicated above, but inasmuch as indices on six horizontal axes are to be considered, the following values will be sought:

$$\frac{h}{l}, \quad \frac{k}{l}, \quad \frac{(h+k)}{l}, \quad \frac{(h+2k)}{l}, \quad \frac{(2h+k)}{l}, \quad \frac{(h-k)}{l}.$$

Although the familiar transformation formula from the standard to the alternative orientation is involved, no further reference to this will be made, but in the gnomonic projection (Fig. 3), these values will be shown as multiples of c/a and $c/\sqrt{3}a$, together with their reciprocals in the linear projection which are directly connected in Fig. 4 with the intercepts on the axes in Fig. 2.

GNOMONIC CALCULATION OF c/a AND $c/\sqrt{3}a$

In the accompanying projection (Fig. 3), we have the gnomonic projection of the forms $c\{0001\}$, $o\{11\bar{2}2\}$, $p\{10\bar{1}1\}$, $s\{11\bar{2}1\}$, $v\{21\bar{3}1\}$, $m\{10\bar{1}0\}$, $a\{11\bar{2}0\}$, and $i\{21\bar{3}0\}$ of beryl with zone lines parallel to the a axes in the front half. In the rear half is shown the linear projection of the face (2131) $A'F'$, passing through the origin 5 cm. below the plane of projection. The graphical solution will at once be clear to those who know that $\tan \rho(1\bar{2}12) = c/a$ and $\tan \rho(10\bar{1}2) = c/\sqrt{3}a$.

Dropping perpendiculars from H , (2131), to each of the six axes, we have $PA = c/a$, $PB = 4c/\sqrt{3}a$, $PC = 3c/a$, $PD = 5c/\sqrt{3}a$, $PE = 2c/a$, and $PF = c/\sqrt{3}a$. This is an extension of Ford's (1922) graphical determination of h , k , and i .

For the complete mathematical calculation, six angles of azimuth are used: ϕ_1 , $(21\bar{3}0) \wedge (2\bar{1}\bar{1}0)$, $\phi_1' = 90^\circ - \phi_1$, ϕ_2 , $(21\bar{3}0) \wedge (1\bar{2}\bar{1}0)$, $\phi_2' = 90^\circ - \phi_2$, ϕ_3 , $(21\bar{3}0) \wedge (11\bar{2}0)$ and $\phi_3' = 90^\circ - \phi_3$.

The cosine of each of the ϕ angles is multiplied by $\tan \rho$ to obtain $\tan \eta$, the tangent of the angle of slope of the three zones involved, and the cosine of each of the ϕ' angles is used similarly to obtain $\tan \xi$, the angle of slope of the other three zones involved with axial ratios, e.g. $\cos \phi_2 \cdot \tan \rho = \tan \eta_2$, the angle of slope of $[21\bar{3}1, 10\bar{1}0]$, whose zone axis is

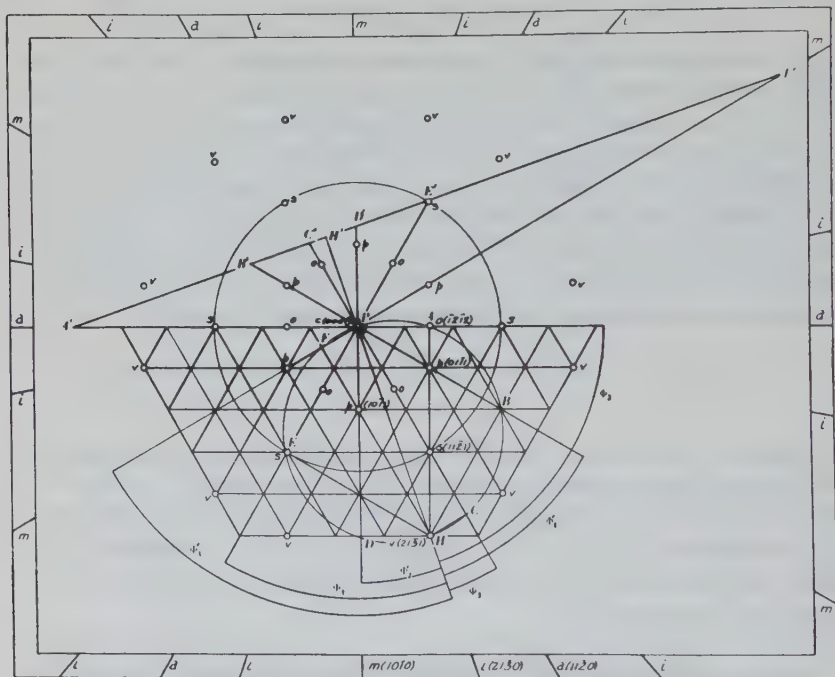


FIG. 3

$[\bar{1}2\bar{1}2]$. This form for the equation involved was apparently first used by Lewis (1899, pp. 428 and 449) for the pyramid $(01\bar{1}1)$ but was not extended to the general case.

This fundamental calculation is the one from which all other gnomonic constants are derived by multiplication or division by a constant, and is the only one that gives the polar constants as reciprocals of the intercepts on the linear axes. The complete calculation for $(22\bar{3}1)$ follows:

$$\cos \phi_2 \cdot \tan \rho = PA/PH \cdot PH/r_0 = \tan \eta_2 = k/l \cdot c/a = l/PA' = r_0/PA' \quad (1)$$

$$\cos \phi_1' \cdot \tan \rho = PB/PH \cdot PH/r_0 = \tan \xi_1 = (h+2k)/l \cdot c/\sqrt{3}a = l/PB' = r_0/PB' \quad (2)$$

$$\cos \phi_3 \cdot \tan \rho = PC/PH \cdot PH/r_0 = \tan \eta_3 = \frac{(h+k)}{l} \cdot c/a = l/PC' = r_0/PC' \quad (3)$$

$$\cos \phi_2' \cdot \tan \rho = PD/PH \cdot PH/r_0 = \tan \xi_2 = \frac{(2h+k)}{l} \cdot c/\sqrt{3}a = l/PD' = r_0/PD' \quad (4)$$

$$\cos \phi_1' \cdot \tan \rho = PE/PH \cdot PH/r_0 = \tan \eta_1 = h/l \cdot c/a = l/PE' = r_0/PE' \quad (5)$$

$$\cos \phi_3' \cdot \tan \rho = PF/PH \cdot PH/r_0 = \tan \xi_3 = \frac{(h-k)}{l} \cdot c/\sqrt{3}a = l/PF' = r_0/PF' \quad (6)$$

These final results are shown graphically in a single plane in Fig. 4, where

$$r_0/PA' : r_0/PE' : r_0/PC' = c/P'A'' : c/P'E'' : c/P'C''$$

and

$$P'A'' : P'E'' : P'C'' \text{ (Fig. 4)} = P'A'' : P'E'' : P'C'' \text{ (Fig. 2)}$$

and

$$r_0/PF' : r_0/PB' : r_0/PD' = c/P'F'' : c/P'B'' : c/P'D''$$

and

$$P'F'' : P'B'' : P'D'' \text{ (Fig. 4)} = P'F'' : P'B'' = P'D'' \text{ (Fig. 2)}$$

LINEAR CALCULATION OF a/c AND $3a/c$

The line $A'F'$ (Fig. 3) is the linear projection of $(21\bar{3}1)$ with the origin below the plane of projection ($r_0=1$). The calculation of the elements concerned follows:

$$\tan (90^\circ - \rho)/\cos \phi_2 = (PH'/r_0)/(PH'/PA') = \tan \eta_2' = \frac{l}{k} \cdot \frac{a}{c} = PA'/r_0$$

$$\tan (90^\circ - \rho)/\cos \phi_1' = (PH'/r_0)/(PH'/PB') = \tan \xi_1' = \frac{l}{h+2k} \cdot \frac{\sqrt{3}a}{c} = PB'/r_0$$

$$\tan (90^\circ - \rho)/\cos \phi_3 = (PH'/r_0)/(PH'/PC') = \tan \eta_3' = \frac{l}{h+k} \cdot \frac{a}{c} = PC'/r_0$$

$$\tan (90^\circ - \rho)/\cos \phi_2' = (PH'/r_0)/(PH'/PD') = \tan \xi_2' = \frac{l}{2h+k} \cdot \frac{\sqrt{3}a}{c} = PD'/r_0$$

$$\tan (90^\circ - \rho)/\cos \phi_1 = (PH'/r_0)/(PH'/PE') = \tan \eta_1' = \frac{l}{h} \cdot \frac{a}{c} = PE'/r_0$$

$$\tan (90^\circ - \rho)/\cos \phi_3' = (PH'/r_0)/(PH'/PF') = \tan \xi_3' = \frac{l}{h-k} \cdot \frac{\sqrt{3}a}{c} = PF'/r_0.$$

The final results are in every case reciprocal to the results of the gnomonic calculation and establish definitely that the linear constants are a/c and $\sqrt{3}a/c$ and that the reciprocal polar constants of the gnomonic projection are c/a and $c/\sqrt{3}a$.

With the introduction of the circle with radius of r_0 , the linear projection assumes importance in helping to solve crystallographic problems and is worthy of further investigation, particularly in the inclined systems.

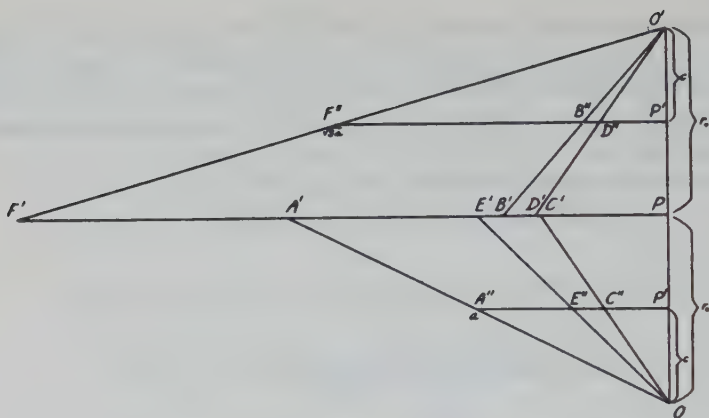


FIG. 4

FOR PRISMS

The calculation of the indices for prismatic faces is as follows:

$$\cos \phi_1 : \cos \phi_2 : \cos \phi_3 = h : k : i.$$

ABRIDGEMENTS TO THE CALCULATION

It is well to let the student see at least one complete calculation which will show definitely the relationship between indices and parameters on all seven axes, and then abridgements to the calculation may well be introduced, depending altogether on what is desired. Equations 1, 3, and 5, give the complete calculation for the crystal when referred to the four standard axes of reference. If only the best average values of c/a and $c/\sqrt{3}a$ are desired, equations 3 and 4 should be sufficient. If indices are desired for forms where l is large or for forms which cannot be readily be shown on the projection, equations 1 and 5 give $k/l \cdot c/a$ and $h/l \cdot c/a$, from which all other desired indices can be derived.

The student will be perfectly satisfied with such an abridgement, whereas he is never satisfied with the explanation that one of the indices has been lost in the projection but can be obtained by adding the two others.

Equation for $\tan \rho$ ($hki\bar{l}$)

From equations (1) and (4), we find

$$\tan \rho(hki\bar{l}) = \sqrt{\frac{k^2c^2}{l^2a^2} + \frac{(4h^2 + 4hk + k^2) \cdot c^2}{l^2} \cdot \frac{c^2}{3a^2}} \quad (7)$$

and from equations (2) and (5)

$$\tan \rho(hk\bar{l}) = \sqrt{\frac{h^2 + 4hk + 4k^2}{l^2} \cdot \frac{c^2}{3a^2} + \frac{h^2c^2}{l^2a^2}} \quad (8)$$

and from equations (3) and (6)

$$\tan \rho(hk\bar{l}) = \sqrt{\frac{(h^2 + 2hk + k^2)}{l^2} \cdot \frac{c^2}{a^2} + \frac{(h^2 - 2hk + k^2)}{l^2} \cdot \frac{c^2}{3a^2}} \quad (9)$$

Each of these equations when reduced to a common denominator and simplified, gives

$$\begin{aligned} \tan \rho(hk\bar{l}) &= \sqrt{\frac{4(h^2 + hk + k^2)}{l^2} \cdot \frac{c^2}{3a^2}} \\ &= \frac{2\sqrt{h^2 + hk + k^2}}{l} \cdot \frac{c}{\sqrt{3}a} \end{aligned} \quad (10)$$

which is the equation of $\tan \rho$ when referred to three sets of orthorhombic axes with ratios $a:\sqrt{3}a:c$. It is simultaneously the equation for a circle having $\tan \rho$ as its radius and the equation for the diameter ($=\tan \rho$) of a circle in terms of its supplementary chords. The first of these is extremely useful in analyzing the results of measurement in terms of $2c$ and $2c/\sqrt{3}$, while the second gives the polar elements c and $c/\sqrt{3}$ directly.

GRAPHICAL DETERMINATION OF POLAR CONSTANTS FROM THE EQUATION FOR $\tan \rho$

In the gnomonic projection (Fig. 3), with $PH = \tan \rho(21\bar{3}1)$ as diameter, describe the circle $PABCDEF$ cutting the six axes at A, B, C, D, E , and F . Then $PA = c/a$, $PB = 4c/\sqrt{3}a$, $PC = 3c/a$, $PD = 5c/\sqrt{3}a$, $PE = 2c/a$, and $PF = c/\sqrt{3}a$.

The polar units derived in this manner are c/a and $c/\sqrt{3}a$: they are the polar units of a hexagonal crystal treated as a special case of the orthorhombic system.

ORIENTATION OF THE PROJECTION

In the hexagonal system there are two types, one giving a triangular pattern in the gnomonic projection, the other an hexagonal pattern. For the first of these, the rhombohedral, it is only necessary to draw the principal zone lines which are parallel to the a axes, having the apex of the inner triangle ($10\bar{1}1$) to the front.

The second is more complicated, but, in general, the zone lines with the greatest number of projection points are perpendicular to the a axes. If there are only first order pyramids, or second order pyramids, or dihexagonal pyramids, the orientation cannot be established beyond question. Any two of these ordinarily can establish the orientation beyond reasonable doubt, so as to give the simplest indices for all the forms.

An interesting exception to both these statements is exhibited in a crystal of hematite described by Foshag (1920) which, except for triangular markings on the base, exhibits perfect hexagonal symmetry and shows $(10\bar{1}1)$ and $(01\bar{1}1)$ truncating the edges of (2243) .

POLAR AND AUXILIARY CONSTANTS

The calculation of the axial ratios and polar constants c/a and $c/\sqrt{3}a$ brings us to the common point where all theories of axial relations in the hexagonal system meet. If we go no further, it leaves us in the position of considering the hexagonal system as a special case of the orthorhombic system. Graphically, these constants have been determined as units of measure of chords of a circle. Three other circles give three pairs of constants, two of which are definitely connected with theories of axial relations while the third seems to be more general in scope. In addition, zone lines drawn perpendicular to any pair of a axes or $\sqrt{3}a$ axes give grids in terms of the polar constants $p_0(G_1)$ or $p_0(G_2)$.

The four pairs of polar constants are as follows:

(1) Hexagonal heptaxial polar constants $c/3a$ and $c/3\sqrt{3}a$ derived by describing a circle with diameter equal to $\tan \rho/3$ thus cutting the six axes at one-third the distance obtained for the orthorhombic constants. The six abscissae taken in any order and moved parallel with themselves, when necessary, locate the projection point of the face normal by co-ordinates in six directions.

(2) Hexagonal tetraaxial polar constants p_0 and Π_0 (Goldschmidt 1886), derived by describing a circle with diameter equal to $2 \tan \rho/3$, thus cutting the six axes at two thirds the distance obtained for the orthorhombic constants. Alternate abscissae give two sets of three which locate the projection point by co-ordinates in three directions as shown by the writer (1938) for p_0 , although as a matter of fact, $p_0(G_2)$, which is arithmetically equal, was used. Goldschmidt could have obtained these constants only from the polar equation of a plane derived from the equation of the plane in terms of the intercepts on four hexagonal axes. This was verified independently for the writer many years ago by Dean Samuel Beatty, Professor of Mathematics in the University of Toronto, but until the simple method described above was found, the writer could see no way of deriving these constants with their proper indices by graphical methods.

(3) Orthorhombic polar constants c/a and $c/\sqrt{3}a$. These have already been shown.

(4) The polar constants $p_0(G_1)$ and $p_0(G_2)$ (Goldschmidt 1886) best derived by drawing zone lines perpendicular to any pair of a axes for $p_0(G_1)$ and any pair of $\sqrt{3}a$ axes for $p_0(G_2)$. These locate the projection

point of the face normal by co-ordinates on *two* inclined axes.

An extremely useful pair of auxiliary constants, $2c/a$ and $2c/\sqrt{3}a$, is obtained from abscissae on the zone lines, which intersect in the projection point of $(hki\bar{l})$, when cut by a circle with radius equal to $\tan \rho$. When $r_0 = 5$ cm., we get direct measurement of c/a and $c/\sqrt{3}a$ as units of measurement of interfacial spacing in the zones shown in the gnomonic projection.

It will be noted that only one pair of the four pairs of polar constants is referred to alternative sets of three horizontal axes and belongs to the hexagonal system, as ordinarily presented. These and the heptaxial constants are polar only in the sense that they locate the projection point of the plane $(hki\bar{l})$ by co-ordinates in three of six directions, respectively, in the gnomonic projection. In every other respect, they must be looked upon as auxiliary constants. When more than two horizontal axes are involved, the projection units for locating the projection point of $(hki\bar{l})$ will be fractions of the normal polar units.

SUMMARY

The reciprocal relations of linear and polar constants in the hexagonal system are shown graphically in linear and gnomonic projections and the complete mathematical calculation from ϕ and ρ angles is given for each projection, with suggested abridgements for ordinary use. The calculations are based on the conception that an hexagonal crystal should be referred to three sets of orthorhombic axes, seven axes in all. Polar constants which have been proposed in the past introduce unnecessary sources of error and should be discarded as a means of calculating axial ratios.

$$\tan \rho = \frac{2\sqrt{h^2 + hk + k^2}}{l} \cdot \frac{c}{\sqrt{3}a}.$$

The polar constants c/a and $c/\sqrt{3}a$ with their proper indices are determined graphically by chords of a circle with $\tan \rho$ as diameter, which in the gnomonic projection is the reciprocal of the trace of the given plane in the linear projection. Two other pairs of polar constants are derived by drawing circles with diameter of $\tan \rho/3$ and $2 \tan \rho/3$ and a fourth pair by drawing zone lines perpendicular to any pair of a axes or $\sqrt{3}a$ axes. The linear projection with the addition of a circle with radius $r_0 = 1$ is shown to be well adapted to two-circle calculations in systems which can be referred to rectangular axes, and when referred to the same origin as the gnomonic projection gives reciprocal relations which are easily recognized. Zonal axes in the linear projection are located by the intersection of the traces of planes having a common horizontal intercept;

zone lines in the gnomonic projection, which are parallel to the $\sqrt{3}a$ axes, connect the projection points of faces having a common h/l , k/l , or i/l and furnish the best means of orientating the projection, the lines with the greatest number of faces being parallel with the a axes in the rhombohedral group and perpendicular to the a axes in crystals with six-fold symmetry.

In conclusion, the writer would pay high tribute to Miller, Goldschmidt, G. F. H. Smith, Lewis, Palache, and Ford, for their contributions to two-circle goniometry. The only changes introduced in their fundamental equations, which are arithmetically correct, involve, in some cases for graphical clarity, the substitution of $1/\tan \rho$ or $\tan (90^\circ - \rho)$ for $\cot \rho$; $\cos (90^\circ - \phi)$ for $\sin \phi$; and $1/\cos (90^\circ - \phi)$ for $\operatorname{cosec} \phi$.

He would also thank Dr. E. H. Kraus, of the University of Michigan, Dr. W. A. Wooster and Dr. F. Coles Phillips, of the University of Cambridge for references establishing the date of the original Miller two-circle goniometer, which preceded the instrument seen by the writer. Finally, he would thank Dr. E. W. Nuffield, of the University of Toronto for making the drawings which illustrate this paper.

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BRAUNITE FROM SNOWMASS, PITKIN COUNTY, COLORADO*

AUSTIN F. ROGERS, *Stanford University, California.*

ABSTRACT

Braunite, tetragonal, with the probable composition $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$, a comparatively rare mineral in this country, is recorded from a new locality in Pitkin County, Colorado.

It is a massive, somewhat granular, black metallic mineral which shows in cavities the pseudo-octahedral crystals highly characteristic of it.

Associated minerals are calcite, barite, a pleochroic mica [probably manganophyll (manganian biotite)], muscovite, quartz, microcline, and plagioclase. The three latter and probably the muscovite are detrital.

Calcite and barite are "persistent minerals" and thus give no clue to the type of deposit, but the presence of manganophyll points to a hydrothermal origin.

Attention is called to the importance of plane angles of crystal faces in the determination of minerals. Plane angles may be expressed as interzonal angles since edges of crystal faces are parallel to the corresponding zone-axes.

INTRODUCTION

Braunite, a characteristic mineral of the manganese ores of India, Sweden, and Brazil, is usually considered to be a rather rare mineral in the United States, although at least eleven American localities have been recorded to date. These are: Cartersville, Ga. (1); Batesville, Ark. (2); Mason County, Tex. (3); Iron County, Mo. (4); Shannon County, Mo. (4); Humboldt County, Calif. (5), Plumas County, Calif. (5), Stanislaus County, Calif. (6), Bisbee, Ariz. (6), Aroostook County, Me. (6), and Golconda, Nev. (6).

The purpose of this article is to put on record braunite from another American locality. I am indebted to Mr. L. P. Teas, consulting geologist, of Houston, Texas, for the specimens herein described.

According to Mr. Teas, the manganese ores were collected from a prospect on a hill one-half mile northwest of Snowmass Post Office, which is about fifteen miles northwest of Aspen, in Pitkin County, Colorado. The prospect is located about 250 feet above the Roaring Fork River. The ore occurs in the Maroon Formation (chiefly Pennsylvanian) in an irregular vein-like deposit from one to five feet thick which transgresses the bedding plane at a small angle. Basalt flows occur a few miles distant.

The information contained in the preceding paragraph was supplied by Mr. Teas in August, 1940; what progress has been made in the development of the deposit I have yet to learn.

* Read by title at the 26th Annual Meeting of The Mineralogical Society of America, Pittsburgh, December 27, 1945.

In the map of structural trends in northwestern Colorado drawn by Macquown (7), Snowmass Post Office must lie on or near the Castle Creek Fault Zone.

Dr. Tom S. Lovering† informs me that there are many occurrences of manganese ore at the base of the basalt flows to the northwest of the locality under discussion.

DESCRIPTION OF THE BRAUNITE

The specimens submitted to me consist of a massive, somewhat granular, iron-gray to black mineral of rather high specific gravity. The streak is brownish black and the mineral is slightly harder than a knife blade. It is very slightly magnetic.

Minute (*ca.* $\frac{1}{4}$ mm.) euhedral crystals are present in cavities. The octahedral appearance of these crystals, together with the slightly magnetic character, suggested braunite, and such they proved to be. The importance of geometrical crystallography in the sight determination of minerals is sometimes overlooked.

A broken surface shows numerous cleavages and since some of these have more or less the shape of equilateral triangles, the cleavage is evidently parallel to the common tetragonal dipyrmaid.

Thin slices of the massive braunite show euhedral to subhedral crystals with sections that remind one of magnetite (see Fig. 1). Chains of subhedral crystals are frequently prominent. The mineral is opaque; this fact distinguishes it from hausmannite, which is decidedly red-brown in thin sections, especially when examined in direct sunlight between crossed nicols (8).

CHEMICAL AND PYROGNOSTIC TESTS

The powdered mineral is soluble in hot dilute hydrochloric acid with the evolution of chlorine which is recognized by its pungent odor and bleaching action of litmus paper, and it also leaves a residue of gelatinous silica.

It gives a good amethyst-colored borax bead in O.F. which becomes almost colorless in R.F.

ASSOCIATED MINERALS

Judging from the thin sections, not more than 60 to 70 per cent or so of the specimens by volume is braunite (see Fig. 1). Hausmannite is a common associate of braunite, as at Långban, Sweden (9), but none could be detected in the Snowmass specimens. The interstitial minerals are mainly calcite and barite; the latter is recognized by its rather weak

† Personal communication, February 2, 1946.

birefringence, fairly high relief in balsam, and an index of refraction of about 1.64, which was determined in fragments by means of immersion liquids.

Several detrital minerals also are present, among them microcline, plagioclase, and quartz. Tabular crystals of muscovite, often curved and bent, are detrital for the most part, but some may be authigenic.

The sedimentary rock containing the braunite may be classified as arkose.

Since both calcite and barite are "persistent minerals" with a wide temperature range, these give no certain clue to the type of deposit. Lindgren (10) does not include barite in his list of "persistent minerals"

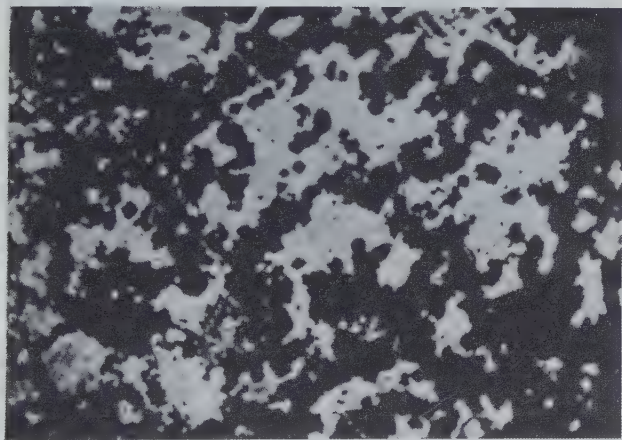


FIG. 1. ($\times 27$). Mineralized arkose with braunite (opaque), interstitial barite and calcite, and muscovite shred (n.w. of center).

but the presence of barite in the rocks of the gondite series of India, as reported by Fermor (11) is, in my opinion, sufficient warrant for extending the temperature range of barite to include hypothermal deposits, since gondite is a metamorphic rock consisting of varying amounts of quartz and spessartite (garnet). According to Butler and Burbank (12), barite reaches its maximum development in mesothermal deposits. Braunite itself has an appreciable temperature range; it is considered to have been formed under conditions varying from metamorphic through hydrothermal to weathering.

The presence of muscovite might be used as an argument in favor of the hydrothermal origin of the deposit, but it is not certain that any of the muscovite is authigenic.

Manganophyll is a characteristic mineral of the Långban manganese deposits (9, pp. 46-48) and occurs there in association with braunite.

A brown pleochroic mica which resembles manganophyll* (manganian biotite) occurs sparingly through the thin sections (see Fig. 2); this is evidence that the braunite is a hydrothermal mineral.

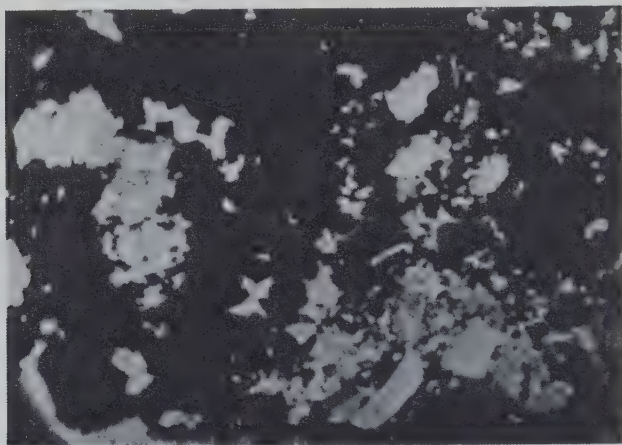


FIG. 2 ($\times 37$). Mineralized arkose with braunite (opaque), interstitial barite and calcite (gray), several detrital grains, muscovite shred (near center), and manganophyll (dark gray, bottom center).

GEOMETRICAL CRYSTALLOGRAPHY

The euhedral braunite crystals of the Snowmass occurrence are minute (about $\frac{1}{4}$ mm.), but distinct enough to be recognized with a hand lens as octahedral or pseudo-octahedral. The crystals are simple tetragonal dipyrramids occasionally modified by the pinakoid $\{001\}$. In the original orientation of Haidinger this dipyramid was taken to be $p\{111\}$ as shown in Fig. 3; down to the end of the nineteenth century this was generally accepted.

The change of orientation of the first order dipyramid $\{111\}$ (Fig. 3) to the second order dipyramid $\{101\}$ (Fig. 4) is credited to Goldschmidt (13) by Hewett and Schaller (3), but Brooke and Miller (14) were the first to make this change. Figure 5 is a copy of Brooke and Miller's drawing, which is a plan view with the forms $e\{101\}$, $s\{201\}$, and $c\{001\}$. This drawing was overlooked by Goldschmidt in his *Atlas der Krystallformen der Mineralien*.

* The original name manganophyll of Igelström is more euphonious than its equivalent, manganophyllite. It also seems a more suitable name since the mineral has no relation to the rock phyllite.

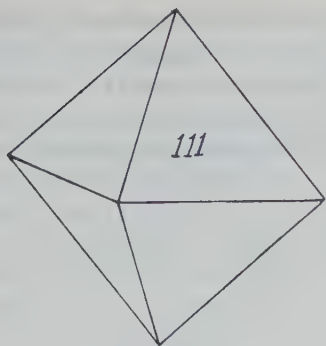


FIG. 3.

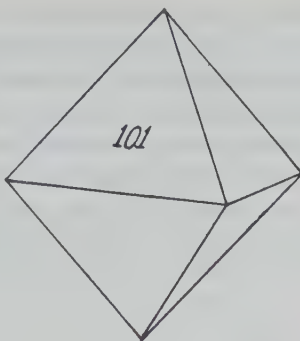


FIG. 4.

FIG. 3. Usual habit of braunite {111}. Haidinger-Dana orientation.
 FIG. 4. Usual habit of braunite {101}. Brooke and Miller—Goldschmidt orientation.

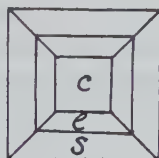


FIG. 5. Plan view of braunite crystal with the forms: $c\{001\}$, $e\{101\}$, and $s\{201\}$. (After Brooke and Miller.)

The transformation scheme of the original Haidinger setting (hkl) to the Brooke and Miller setting (pqr) is as follows:

$$\begin{array}{lll} \text{(Haidinger)} & hkl & \rightarrow h-k \cdot h+k \cdot 2l \\ & p+q \cdot q-p \cdot r & \leftarrow pqr \quad \text{(Brooke and Miller).} \end{array}$$

This change of one setting to the other is the equivalent of a rotation of 45° and modification of the unit on the c -axis by $\sqrt{2}$.

Expressed in the linear form of Barker the transformation scheme is $110/\bar{1}10/002$ (D. to G.) and $\bar{1}10/110/001$ (G. to D.) as given by Switzer (15), who designates the two settings as Dana (D.) and Goldschmidt (G.).

Three kinds of angles are recognized in solid geometry:

- (1) Plane angles of the faces.
- (2) Dihedral or angles over the edges.
- (3) Polyhedral or solid angles at the vertices.

Polyhedral angles may be resolved into a combination of plane angles and dihedral angles. In crystallography dihedral angles are called interfacial angles. Donnay and O'Brien (16) designate plane angles of crystal faces as interedge angles.

Plane angles were formerly recorded in books on geometrical crystallography; because of the difficulty of accurate measurement of these angles the custom fell into disuse. It is my contention (17) that plane angles are used unconsciously in the sight-determination of crystallized minerals more than interfacial angles. For example, we probably recognize small quartz crystals by the shape of the triangular r faces rather than by interfacial angles such as mr . The plane angle of the r face at the apex of the usual $rz\bar{m}$ combination is $41^\circ 51'$. See Fig. 1, p. 8, reference (18).

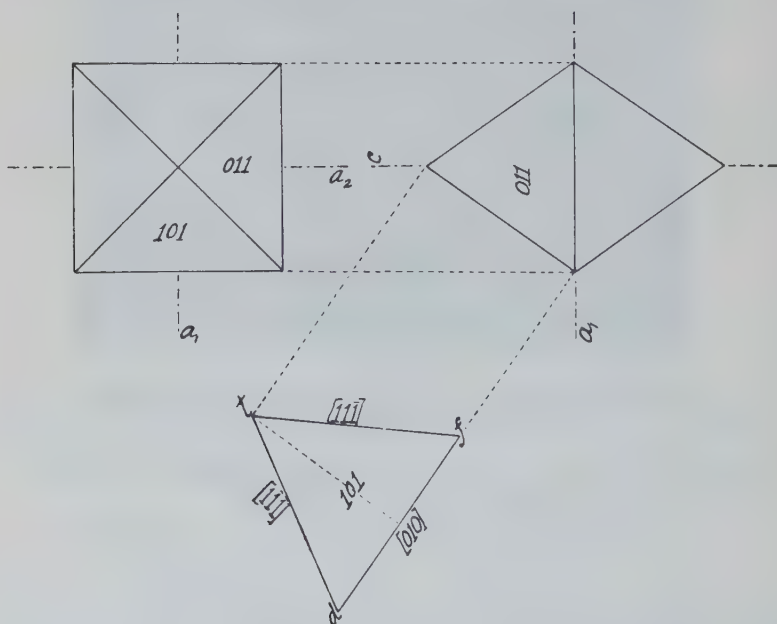


FIG. 6. Graphic determination of plane angle $dtf = [11\bar{1}] \wedge [\bar{1}11]$ on a braunite crystal with the $\{101\}$ form.

The graphic determination of plane angles is accomplished by constructing a projection (19) so that the face appears in its true shape (19). For braunite we first construct (Fig. 6) a plan view on the left, then the side elevation from the interfacial angle ($101 \wedge 10\bar{1} = 70^\circ 48'$). To show the (101) face in its true shape we construct a supplementary projection with folding-line parallel to the $[101:011]$ edge by making the edge df $[010]$ equal to the corresponding edge in the plan. In the triangle dtf the angle dtf is very close to 60° . This plane angle may be expressed as the interzonal angle $[11\bar{1}] \wedge [\bar{1}11]$. The calculated value of this angle is

$60^{\circ}10'$,* if we use the ρ angle of $(011) = 54^{\circ}36'$ determined by Switzer (15). The other plane angles $[1\bar{1}\bar{1}] \wedge [010]$ and $[11\bar{1}] \wedge [010]$ are each $59^{\circ}55'$. So the common form $\{101\}$ of braunite is decidedly pseudo-octahedral. The plane angle at the apex of the usual hausmannite crystal with the unit dipyrmaid $\{111\}$ is $54^{\circ}34'$, which is the same as the interzonal angle $[10\bar{1}] \wedge [01\bar{1}]$.

THE CHEMICAL COMPOSITION OF BRAUNITE

Perhaps the most interesting, and certainly the most puzzling, feature of braunite is its chemical composition. This was formerly given as Mn_2O_3 , but to account for the silica, which is present to the amount of about ten per cent, the formula is usually given as $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$. Rammelsberg (20) was the first to suggest this formula. An analysis of the Långban braunite by Flink (21) furnished confirmation of this formula. Niggli (22), however, expresses the composition as $n\text{Mn}_2\text{O}_3 \cdot m\text{MnSiO}_3$ because of the supposed variability in the silica content. Ford (23) writes the formula $3\text{MnMnO}_3 \cdot \text{MnSiO}_3$. Palache, Berman, and Frondel (24) suggest the possibility of the replacement of manganese by silicon as expressed by the formula $(\text{Mn},\text{Si})_2\text{O}_3$.

Another variation in the chemical composition is the presence of ferric iron replacing the trivalent manganese which gives the formula $3(\text{Mn},\text{Fe})_2\text{O}_3 \cdot \text{MnSiO}_3$ proposed by Hewett and Schaller (3). The ferrian braunite of Mason County, Texas, contains as much as 15 per cent Fe_2O_3 (3), but analyses of braunite from other localities show less than one per cent Fe_2O_3 . Strunz (25) places braunite in a group with bixbyite $(\text{Mn},\text{Fe})_2\text{O}_3$.

Mason and Byström (27) call attention to an analysis of braunite from Kájlidongri, India, mentioned in the paper of Fermor (11, p. 68) which furnishes the formula $3\text{Mn}_2\text{O}_3 \cdot (\text{Mg},\text{Ca})\text{SiO}_3$. This is confirmation of the formula of Rammelsberg.

The synthesis of braunite from Mn_2O_3 and MnSiO_3 by Mason and Byström is additional confirmation of the formula $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$.

The probable space-group of braunite was determined by Aminoff (26) to be D_{4h}^{20} . Mason and Byström (28), however, give arguments in favor of the space-group D_{2d}^{10} , which means that the crystal class is tetragonal-scalenohedral. But since none of the figured braunite crystals show any sign of merosymmetry their conclusion is open to question.

The complete structure of braunite has not yet been solved, which is not surprising in view of Aminoff's statement that 160 atoms are present in the unit cell.

* The equation is: $[1\bar{1}\bar{1}] \wedge [11\bar{1}] = 2 \text{ arc cot } \{ \sec (001 \wedge 011) \}$.

ACKNOWLEDGMENTS

I am indebted in the first place to Mr. L. P. Teas for the specimens of braunite which furnish the material for this paper; to Mr. Alexander Tihonravov, Department Technician, for the photomicrographs; and to Dr. Tom S. Lovering for valuable suggestions.

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EFFECT OF TEMPERATURE ON LINEAGE STRUCTURE IN SOME SYNTHETIC CRYSTALS

O. F. TUTTLE AND W. S. TWENHOFEL, *Naval Research Laboratory,
Washington, D. C.*

ABSTRACT

Experiments on the growth from solution of large synthetic crystals of lithium sulfate monohydrate ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) demonstrate that lineage structure and attendant cracking in the crystal are eliminated if the crystals are grown at about 94°C . Crystals grown at lower temperatures have considerable lineage structure and are profusely cracked. Earlier theories as to the cause of lineage structure are reviewed and a new theory is presented. It is concluded that increased thermal agitation of the units being added to the growing crystal permit a more ordered arrangement of the atoms that make up the crystal structure.

INTRODUCTION

Geologists and mineralogists are familiar with the fact that characteristics of minerals of the same species differ widely according to the geologic environment in which they are formed. In many cases such differences have been correlated qualitatively with differences in the composition, temperature, pressure, and pH of the depositing solutions. Few workers, however, have marshalled much quantitative or direct experimental evidence in support of their conclusions. The authors contend that many of the features of natural crystals can be duplicated in the laboratory, and knowledge of the factors that control habit, physical properties, electrical properties, and structure of synthetic crystals will undoubtedly lead to a more thorough understanding of the conditions of formation of natural crystals. A relation between the amount of defects and the temperature of formation of pyrite crystals has been postulated by Smith.¹ Pyrite from low temperature deposits commonly shows an extreme development of lineage structure whereas a pyrite crystal from a higher temperature deposit will have less imperfections and lineage structure may not even be recognizable. A similar relationship has been found in synthetic crystals grown recently at the Naval Research Laboratory.

The faces of many crystals are made up of many small units with slightly different orientations. Buerger² recognized that these small sub-units are not separate unrelated units, but that they can be traced back to the original nucleus or seed; consequently he proposed the term lineages for these structures, "... whose orientation descend continuously

¹ Smith, F. G., Lineage structure and conditions of deposition of pyrite: *Econ. Geol.*, **37**, 519-523 (1942).

² Buerger, M. J., The significance of "block structure" in crystals: *Am. Mineral.*, **17**, 177-191 (1932).

from the same parent nucleus but whose orientations may differ." The surface between two such structures is, then, a lineage boundary, which may be an actual break or crack in the crystal.

While making a detailed study of some electrical properties of pyrite Smith³ found that the degree of development of lineage structure greatly affected the electrical properties and that the temperature of formation of pyrite apparently could be correlated with the degree of development of the lineage. Laboratory synthesis of crystals under controlled conditions affords proof that crystal imperfections such as lineage and lineage cracks are related to temperature as Smith postulated.

EFFECT OF TEMPERATURE

Large crystals of lithium sulfate monohydrate ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) have been grown from solution at temperatures ranging from 24°C. to 94°C. The crystals were grown at a precisely controlled temperature from a saturated water solution of lithium sulfate. "Seeds" were attached to a rotating rod in the solution and were freely exposed to the solution at all times during growth. The solutions from which the crystals were grown, were, in all cases, essentially identical except for a difference in temperature and consequently a difference in the concentration of the saturated solution. The concentration of a saturated solution of lithium sulfate decreases but slightly with an increase in temperature. Scores of crystals were grown at 24°C., 43°C., and 94°C. Various types of seed crystals were used; some were tiny perfect crystals, others were cut crystal plates without flaws, and still others were badly flawed and cracked crystal plates. The rate of crystal growth was essentially the same at all temperatures.

The phrase, "lineage cracks" is proposed for those cracks obviously related to structural defects. All lineage units are not bounded by cracks, but it is believed that all are potential cracks. A seed with no cracks can be easily grown (at low temperature) up to a crystal 2 or more centimeters on a side without cracking. However, on further growth cracking may begin in the center of the crystal and gradually progress outward. The final crystal may have numerous cracks starting at or near the seed and extending outward toward the surface. They may or may not extend to the surface of the crystal. In other cases cracking may start at the surface and extend inward toward the original seed, in which case the crack will be propagated outward at the surface as the crystal continues to grow. It must be emphasized that cracking of this type is not restricted to lineage boundaries although the strain developed at lineage boundaries initiates cracking which may then cut through the lineage units themselves.

³ Smith, F. G., *op. cit.*

Those crystals grown at 24°C. are traversed by a multitude of small cracks that formed as the crystal grew. Those grown from perfect seeds are only slightly less cracked than those grown from cracked seeds. Lineage structure is also revealed by a slightly different orientation of reflection from crystal faces (see Fig. 1). In some crystals the cracks are confined to the parts of the crystals that show lineage structure. Apparently these cracks are a manifestation of the lineage structure.

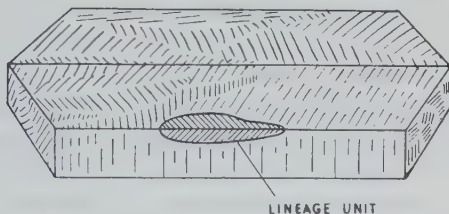


FIG. 1. Sketch of a $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystal showing the effect of lineage structure on the orientation of parts of the crystal faces. The lineage unit can be traced back to the seed crystal. The boundary of a lineage unit with neighboring units may be a break or crack in the crystal. The hachure lines in the sketch are not striations, but are merely a way of diagrammatically showing that the lineage units are of slightly different orientation.

Crystals of lithium sulfate monohydrate grown at 43°C. also are traversed by many cracks and possess lineage structure. The quality of the crystals, however, is somewhat better than those grown at lower temperatures.

Crystals grown at 94°C., irrespective of whether they started from perfect or imperfect seeds, are entirely free of cracks and essentially no lineage structure is discernible.

Several different batches of crystals were grown at the various temperatures and the results were duplicated many times. There can be no doubt that, if factors other than temperature are constant, crystals of lithium sulfate monohydrate grown from solution are more nearly perfect and do not have lineage structure if grown at high temperatures.

DISCUSSION

Buerger⁴ has proposed two causes of lineage structure and the authors propose a third. (1) *Solid solution*: Buerger postulates that foreign atoms in solid solution (a foreign atom proxies for another atom) that are not uniformly arranged within the crystal lattice must cause a structural distortion which may give rise to lineage structure. Buerger⁵ states,

⁴ Buerger, M. J., *op. cit.*

⁵ Buerger, M. J., *op. cit.*, p. 189.

"Unless the crystal is precipitated under equilibrium conditions, its impurity content does not have a chance to acquire a regular distribution."

(2) *Keying of surface cracks*: Buerger⁶ reviews the evidence for the existence and size of submicroscopic cracks that form at the surface of crystals. He states, "The presence of these flaws has been suggested along two main lines of independent evidence; the discrepancies in expected and experimental strengths of solid materials and the calculated surface contraction in ionic crystals."

Convincing evidence for the existence of submicroscopic surface cracks has been presented by Griffith⁷ and Zwicky.⁸ Buerger presents a case for the keying open or plugging of the submicroscopic cracks by the rapid addition of new material either as isolated atoms or as minute crystal blocks. He proposes that rapid growth would cause the atoms or blocks to attach themselves so rapidly that the cracks would be plugged before they were able to close. Submicroscopic surface cracks might also be keyed open by the incorporation of foreign material which would fill or bridge the cracks in the crystal structure. If the foreign atoms were sufficiently large they would keep the crack open and thereby preserve the structural distortion.

(3) *Misoriented minute crystal blocks*: Evidence from a number of different methods of experimentation indicates that crystals grow not by the addition of single atoms (or ions) into the crystal lattice, but rather by the addition of minute crystal blocks or aggregates of atoms that first form in the solution and then are incorporated on the crystal surface.⁹ It is conceivable that not all of the minute crystal blocks would finally come to rest in precisely the correct position for continuation of the ideal crystal structure. Some of the blocks may be too large or the wrong shape to fill a given space between adjacent blocks. Even though the rate of addition of the blocks is very slow it is probable that some of the blocks will not align themselves in their proper place for continuation

⁶ Buerger, M. J., *op. cit.*, p. 182.

⁷ Griffith, A. A., The theory of rupture: *Proc. First Int. Cong. for Applied Mechanics*, Delft, 55-63 (1925).

⁸ Zwicky, F., On the imperfections of crystals: *Proc. Nat. Acad. Sci.*, **15**, 253-259 (1929).

⁹ Volmer, M., Zum Problem des Kristallwachstums: *Zeit. physik. Chem.*, **102**, 267-275 (1922).

Spangenberg, K., Zur Kinetik des Wachstums- und Auflösungs Vorganges von einfachen Ionengittern in wässriger Lösung: *Zeit. Kris.*, **59**, 383-405 (1924).

Volmer, M., and Weber, A., Keimbildung in übersättigten Gebilden: *Zeit. physik. Chem.*, **119**, 277-301 (1926).

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of the crystal lattice. Brandes¹⁰ proposes a similar mechanism to explain some of the anomalous physical properties of some crystals. Certain anomalous properties are assumed by Smith¹¹ and others, to be a manifestation of the degree of orderliness of the crystal structure.

Buerger ascribes lineage structure to crystallization under non-equilibrium conditions (i.e., from a highly supersaturated solution). If the crystal grows from a highly supersaturated solution it may grow so fast that submicroscopic surface cracks are keyed open and added material will come to rest where it first entered the crystal lattice, and the defect may be sealed over before it can be uniformly distributed and oriented in the crystal lattice. If structural distortion is actually caused by misorientation of minute crystal blocks, then too rapid growth may cause the blocks to be covered over before they are reoriented to fit precisely in the crystal lattice.

The authors suggest that the amount of thermal agitation of the materials being added to the crystal, be they single atoms or groups of atoms, is a dominant factor in the development of lineage structure in crystals. Regardless of whether lineage structure is ascribed to foreign materials in solid solution, to the keying open of submicroscopic surface cracks, or to a misoriented grouping of minute crystal blocks, it seems plausible that the material being added to a growing crystal will be more likely to assume a position in harmony with the ideal crystal structure the greater the agitation and energy of the material. The higher the temperature of growth the greater the agitation of the material being added to the crystal. Therefore, crystals grown at high temperatures will have fewer structural defects (less lineage structure) than those grown at lower temperatures. This conclusion is substantiated by the experiments on the growth of crystals of lithium sulfate monohydrate described elsewhere in this paper.

CONCLUSION

It has been demonstrated that for the crystal $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ lineage structure and attendant cracking are essentially eliminated if the crystal is grown at high temperatures. It is concluded that increased thermal agitation at the higher temperatures permits the units that are being added to the crystal to assume a more orderly position in the lattice, whether the lineage be caused by solid solution impurities, by keying open of submicroscopic surface cracks or by a disordered arrangement of groups of atoms on the growing crystal surface.

¹⁰ Brandes, H., *op. cit.*

¹¹ Smith, F. Gordon, Variation in the electrical conductivity of pyrite: *Univ. Tor. Studies*, Geol. Ser., **44**, 83-93 (1940); and Variation in the properties of pyrite: *Am. Mineral.*, **27**, 1-19 (1942).

ORIGIN OF SPHEROIDAL CLUSTERS OF ANALCIME FROM BENTON COUNTY, OREGON

LLOYD W. STAPLES, *University of Oregon, Eugene, Oregon.*

ABSTRACT

An unusual occurrence of analcime has been found at Coffin Butte, Benton County, Oregon. Trapezohedrons of analcime are arranged in spheroidal clusters with hollow centers. Natrolite occurs as acicular prismatic crystals completely enclosed within the analcime. The arrangement of the natrolite indicates that it originally radiated from the now hollow centers of the clusters.

The spheroidal clusters, which often appear only as rings of crystals, are not due to cyclic twinning as has been suspected, but the grouping probably has been controlled by the radiating structure of the natrolite. The steps in the development of a spheroidal arrangement of this type can be seen from a study of perched crystals. With analcime perched on natrolite as a starting point, further growth of the analcime and removal of the unprotected natrolite would produce spheroidal clusters of analcime such as were found at Coffin Butte.

INTRODUCTION

Many fine specimens of zeolites have been obtained from a basalt quarry on Coffin Butte, located about 10 miles north of Corvallis in Benton County, Oregon. The Butte lies adjacent and to the west of U. S. Highway 99 W., and is about one mile south of the Polk county line. It stands out as a prominent topographic feature rising 500 feet above the flood plain of the Willamette River. It is elliptical in plan with its major axis about one mile long and trending northeast-southwest. There are numerous quarries in the Butte from which rock was obtained for road ballast for Camp Adair. The presence of well defined pillow structures with radial jointing in the basalts, and numerous small beds of intercalated sandstone, indicate that the basalt was extruded in several flows with short periods of quiescence between. The age is early Tertiary, probably Eocene.

Well crystallized specimens of stilbite, mordenite, mesolite, natrolite, heulandite, chabazite, apophyllite, and analcime were obtained from veins, brecciated zones, and gas cavities at various localities on the Butte. The best specimens collected to date have come from a quarry at the north east end of the Butte. At this place the deposition was limited to the following, arranged in their order of deposition: natrolite, analcime, stilbite, apophyllite, and finally chabazite.

Among the most interesting of the zeolites from Coffin Butte were clusters of analcime crystals which had been called "cyclic twins" by local collectors. The writer studied these groups of crystals in an attempt to determine their origin.

DESCRIPTION OF CLUSTERS

The individual analcime crystals are trapezohedrons, without modification, varying from about 2 mm. to 12 mm. in diameter, the average being about 5 mm. in diameter. They have low birefringence and an index of refraction of 1.486 ± 0.001 . The analcime shows very irregular double refraction and some complex twinning, often polysynthetic. One type of anisotropism, observed in thin sections, consists of an isotropic cross which divides the area into quadrants with negative elongation. Usually the dark cross maintains a constant position and rotates with the stage, all quadrants extinguishing almost simultaneously. However, in some cases the cross remains parallel to the cross-hairs during the rotation of the stage, as in spherulites. Numerous careful studies have been made on the causes of the anomalous double refraction in analcime, the outstanding pioneer work being that of Ben-Saude (1), and Klein (2). These writers concluded that analcime was isometric and explained the double refraction as being due to internal tension set up as a result of change in temperature. The Coffin Butte analcime provided an opportunity to determine whether mechanically produced strain during growth might play a part in causing the double refraction, since it would be expected that the analcime with inclusions would show the most strain and consequently most double refraction. This was not the case, there being equally as much double refraction in the analcime which had no inclusions.

The clusters of analcime are fairly uniform in size, averaging about 12 mm. in diameter (Fig. 1). Most of the clusters appear to be cyclic, often forming a complete circle with hollow center (Fig. 2). Actually these circular groups are sections of hollow spheroids, and in a few cases almost completely closed spheroids were found.

The clusters rest on a cavity coating of nontronite, and occasionally the nontronite is included in the analcime crystals. The nontronite has a radiating spherulitic structure and shows considerable pleochroism, from deep brown to greenish gray. The maximum and minimum indices of refraction are 1.615 ± 0.003 and 1.574 ± 0.003 on the best material. From other parts of the Butte, material of lower indices of refraction was obtained, indicating the presence of other members of the nontronite-beidellite series. Microchemical tests of the nontronite showed the presence of large amounts of magnesium, iron, and silicon, with smaller amounts of calcium and aluminum. The nontronite was probably derived from the basaltic glass, which commonly forms crusts around the basalt pillows, and then migrated to its present location under conditions such as described by Allen and Scheid (3). Although most of the nontronite was deposited before the formation of the zeolites, a small

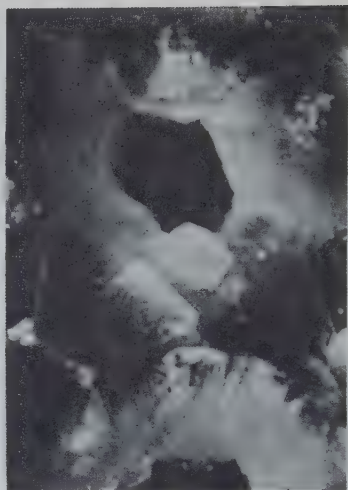


FIG. 1. Spheroidal clusters of analcime from Coffin Butte— $\times 3\frac{1}{2}$.
FIG. 2. Clusters of analcime crystals with natrolite radiating from centers. Coffin Butte— $\times 5$.

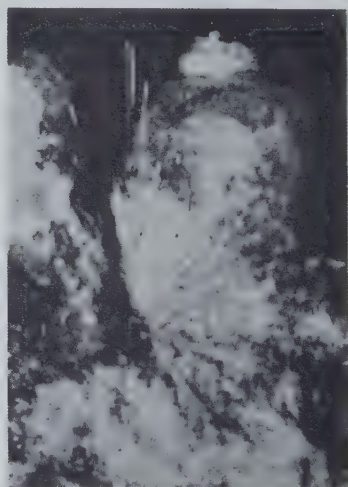


FIG. 3. Analcime perched on natrolite, from Coburg quarry— $\times 30$.
FIG. 4. Radiating group of natrolite crystals partly enclosed by analcime, from Coburg quarry— $\times 5$.

amount came later indicating that the period of migration and deposition was not a short one.

The analcime crystals contain inclusions of a white acicular mineral which radiates from the hollow centers of the spheroidal clusters and produces a white turbid area around these centers, sharply contrasting with the clear colorless areas that are without inclusions (Fig. 1). The enclosed acicular crystals average about 2 mm. in length and in thin section show distinct alteration rims about them. It is probable that this alteration is largely responsible for making the acicular prisms so clearly visible within the analcime (Fig. 2). The alteration makes it difficult to obtain satisfactory Becke line tests. However, oriented sections cut normal to the prism zone give symmetrical extinction and good interference figures, which together with the other optical properties prove the mineral to be natrolite.

A partial spectrographic analysis was made of an analcime crystal with its natrolite inclusions and the result showed less than 1.0% calcium, indicating that both the analcime and natrolite were very low in calcium.

It was observed that in no case were spheroids present without having inclusions of natrolite in them, and in every case the natrolite needles radiated from the hollow centers of the spheroids.

The question as to whether the natrolite pierced or replaced the analcime, was formed at the same time as the analcime, or was enclosed by growth of the analcime is important in any consideration of the origin of the clusters. A suggestion as to the solution of this problem was given by observations on some perched crystals from other localities.

PERCHED CRYSTALS

The perched habit for zeolites and closely related minerals has been considered fairly rare. In a discussion of the minerals of the New Jersey diabase, Levison (4) describes supporting "flexible filaments" of "probably a fibrous natrolite" with "parasitic" crystals of "calcite, datolite, apophyllite or other minerals." Murdoch and Webb (5) mention an unusual case from Red Rock Canyon, California where "... a few sharp natrolite crystals have analcite crystals perched on the natrolite terminations." Recently the unusual occurrence of cristobalite and quartz perched on mordenite has been described from India (6). The writer has found several good examples of perched zeolites recently, such as chabazite perched on mordenite from near New Era, Oregon, and a similar occurrence from Kalama, Washington (Fig. 5). Chabazite also occurs perched on mesolite on the Oak Grove Fork of the Clackamas River, Oregon, and on natrolite at Coffin Butte. Laumontite is found perched

on mesolite at New Era. The most interesting combination from the standpoint of this study was the analcime perched on natrolite from Coburg quarry, located about five miles north of Eugene, Oregon, on the northeast bank of the McKenzie River (Fig. 3).

In the material studied from Coburg quarry, all gradations have been noted from small analcime crystals perched near the top of the natrolite needles, to specimens in which the analcime crystals have diameters almost equal to the length of the natrolite needles. Other specimens show the natrolite in radiating masses with analcime crystals perched in an arc. Figure 4 shows an intermediate stage with analcime enclosing some radiating natrolite crystals while others remain free. It is believed that these perched crystals, and examples of natrolite partly enclosed in analcime, represent a stage through which the spheroidal clusters passed in their formation.

The study of perched zeolites, in addition to its direct bearing on the origin of the analcime clusters, is of interest because of the possibility of deriving data on selective perching as a special type of selective incrusta-

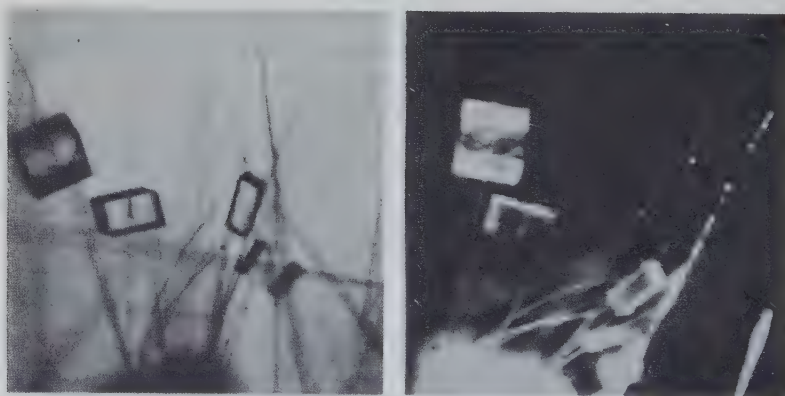


FIG. 5. Chabazite perched on mordenite from Kalama, Washington. Left photomicrograph made with substage lighting. Right with reflected light— $\times 19$.

tion, and directed orientation of crystals. To date, a sufficiently large number of occurrences of perched zeolites have not been found to permit deriving general conclusions, but the careful study of new localities should provide more data.

From the limited number of examples of perched zeolites studied, it appears that almost any combination of zeolites may produce perched crystals, and the acicular zeolites often form mounts for calcite and other non-zeolite minerals.

It was considered possible that there might be some preferred orientation of the perched zeolites on the supporting stalks. In Fig. 3, it appears that the analcime has oriented itself with a 4-fold axis parallel to the natrolite prism zone, and in Fig. 5 there seem to be numerous examples of chabazite rhombohedrons arranging themselves with a face parallel to a mordenite crystal. However, observations on numerous other perched crystals proved there were a great many exceptions to these orientations and no generalizations can be made from this material regarding preferred orientation of the perched crystals.

In the case of two prismatic zeolites, parallel or near parallel growth often takes place. Scheit (7) noted a case of thomsonite enveloping natrolite with the c axes parallel but a very slight non-parallelism of the corresponding thomsonite pinacoids and natrolite prism faces. At Coffin Butte, a good example of crystals of natrolite terminated by mesolite was found. The dividing line between the two species was a sharp angular line and could be seen in ordinary light, although there was no change in the outline of the crystal. Under crossed nicols the difference in birefringence made the change from one species to the other very distinct. At Coburg quarry the relations were reversed and many crystals had a mesolite base and natrolite termination. The lack of gradation between natrolite and mesolite gives further evidence that they are not completely isomorphous.

Penfield (8) studying analcime from the Phoenix Mine, found a secondary growth of analcime in partial parallelism with a core of earlier analcime. Due to the lack of complete parallelism the later analcime tended to break apart into octants.

ORIGIN OF COFFIN BUTTE SPHEROIDAL CLUSTERS

At Coffin Butte, natrolite was deposited at an early stage, in radially arranged acicular crystals. The development of the spheroidal clusters of analcime probably was controlled by the natrolite in the following manner. With a change in the composition of the depositing solutions, marked by an increase in silica and a decrease in alumina and soda, analcime started to grow as perched crystals on the radiating natrolite. Growth of the analcime continued until the trapezohedrons made contact with each other. Where this growth was uniform and from equally spaced centers, almost perfect spheres formed. This was an exceptional condition, and in most cases more irregular spheroidal clusters, or only rings were formed. Oriented thin sections cut normal to the natrolite prisms show the presence of reaction rims which probably formed as the solutions changed and the analcime started to deposit. With continued change in the character of the solutions, the natrolite was no longer in equilibrium

and was completely dissolved except where protected by the enveloping analcime. This resulted in the centers of the spheroidal clusters becoming hollow, and an absence of natrolite protruding from the outer surfaces of the analcime in the clusters. In no case were remnants of natrolite found in the center or projecting out of the spheroids.

Fenner (9) in his description of the zeolites of the Watchung basalt, reports the early formation of analcime and later crystallization of natrolite. He states (p. 165),

The relations of analcite and natrolite are of especial interest because of the inferences derived from the application of the phase rule. It should be found that where the two exist together, one belonged to a period of higher temperature and remained stable until a definite transition point was reached, when it began to pass over into the other. It appears that this is true and that the direction of the change is from analcite to natrolite.

Fenner gives substantial evidence to prove that natrolite has replaced the analcime and he notes that the natrolite looks perfectly fresh while the analcime appears spongy and decomposed. At Coffin Butte the fact that the analcime is later than the natrolite is shown by the clear fresh appearance of the analcime and the alteration rims on the natrolite. The localization of the natrolite at the centers of the analcime clusters would likewise be difficult to explain if the natrolite had not preceded the analcime, since voids between clusters would have provided equally good positions for the attack on the analcime by the natrolite. Finally, the occurrence of analcime perched on natrolite is satisfactory evidence of the earlier formation of the natrolite. Although it is probable that analcime most often precedes natrolite, the reverse order has been recognized in several localities. At Snake Hill, N. J., in diabase closely related to the Watchung basalt, Levison (4) noted the order: "trap, pectolite, natrolite, and analcite." In this case analcime was sequent on natrolite and terminated pectolite, so the order should have been evident even without a microscope. At Coffin Butte, the earlier crystallization of natrolite seems sufficiently well established so that it may safely be used in an explanation of the origin of the spheroidal clusters described in this paper.

CONCLUSIONS

The spheroidal clusters of analcime found at Coffin Butte, Benton County, Oregon, are not cyclic twins but probably have been arranged under the control of the radiating structure of natrolite. The formation of the analcime produced only a mild reaction with natrolite, but further change in the character of the solutions caused complete solution and removal of the latter, except where protected by the analcime.

It is also probable that an intermediate stage in the formation of the

spheroidal clusters was the growth of perched crystals of analcime on natrolite. This perched habit, which has been considered fairly rare, was found to be rather common at the zeolite localities in Oregon.

If the hypothesis of formation stated here is correct, we have another good example of one mineral directing the crystallization of another. There is also evidence of the change in composition of the depositing solutions with preservation of a less stable phase by inclusion in a more stable one, as the character of the solutions changed.

ACKNOWLEDGMENTS

The writer wishes to thank Mr. Lloyd Ruff of the U. S. Army Engineers of Portland, Oregon, and Mrs. Ted Gordon of Salem for specimens for study. He is also indebted to Mr. Louis Artau of the University of Oregon for expert assistance in taking the photographs accompanying this paper, and to Miss E. Miller of the Oregon State Department of Geology and Mineral Industries for a partial spectrographic analysis.

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CHEVKINITE (TSCHEFFKINITE) FROM ARIZONA¹

ALBERT J. KAUFFMAN, JR.² AND HOWARD W. JAFFE.³

ABSTRACT

A new occurrence of chevkinite, a titano-silicate of the rare earths, has been found in Mohave County, Arizona. Petrographic and chemical analyses and the x-ray powder diffraction pattern of this mineral are given. The differences from keilhauite and allanite are shown. Minerals associated with the chevkinite are sphene, monazite, apatite, cronstedtite and quartz.

OCCURRENCE

A new occurrence of chevkinite, a titano-silicate of the rare earths, has been found by L. H. Carson of Seligman, Arizona. The sample, sent to the Bureau of Mines for identification, came from a dike in the Aquarius Mountains, Mohave County, Arizona. Chevkinite previously has been reported from only two localities in this country, Nelson and Bedford Counties, Virginia. A possible additional occurrence, to which the writers cannot find reference in the literature, is Mitchell County, North Carolina. Two samples of chevkinite in the U. S. National Museum are reportedly from this locality; they are from an old collection, and their source cannot be accurately traced. Dr. J. H. Pratt (1916), former State Geologist of North Carolina, states that chevkinite "has been identified in the United States in only one state, Virginia."

The few confirmed foreign localities are widely scattered and include the Ilmen Mountains, Russia; the Salem district of South India; the Tordendrika-Ifasina region of Madagascar; the Kōgendō region of Korea; and Sabaragamuwa Province in Ceylon. According to Carson, the Arizona mineral comes from "a long narrow vein, a few inches to a foot in width, running lengthwise of a high granite dike." Further field information is not available, but the pegmatite veins of the Aquarius Range are well-known; gadolinite, arizonite, samarskite and allanite having been identified in these rocks (*Arizona Bureau of Mines*, 1941). From Carson's brief description, it appears likely that the Arizona sample of chevkinite is also associated with a pegmatite. Very little information on the mode of occurrence of chevkinite is given in the literature. The most reliable study of the field occurrence of this mineral was made by Lacroix (1915). Of the Madagascar material, he writes, "In conclu-

¹ Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior.

² Chemist-Petrographer, Metallurgical Branch, College Park Division, Bureau of Mines, College Park, Md.

³ Petrographer, Metallurgical Branch, College Park Division, Bureau of Mines, College Park, Md.

sion, one finds that at Torendrika-Ifasina, the rare-earth minerals are a production of the magma of an alkaline aegirine granite; they originated in a pegmatitic phase of this."

PHYSICAL AND OPTICAL PROPERTIES

The sample weighed half a pound and contained a few poorly defined crystal faces. It could not be determined whether these belonged to chevkinite or whether this mineral had pseudomorphously replaced another. The mineral is black; possesses a dull luster; and breaks with an irregular fracture. It is slightly radioactive, a function of the thorium content. Uranium was not detected spectrographically or by means of the very sensitive sodium fluoride fluorescent bead test (Northup, 1945). The specific gravity is 4.67 and the hardness 5.5 to 6. In transmitted light the mineral is moderately pleochroic from brown to dark reddish brown, somewhat resembling tantalite-columbite. It shows no distinct cleavage in thin section or fragment. The intermediate index β is 1.99. The mineral is optically negative, with a moderately large axial angle, and shows marked dispersion with $r > v$. The birefringence is moderate. The birefringence and intermediate index are higher than those previously reported for this mineral. These higher values may result from the relatively high ferric iron content of the Arizona material.

Several samples of chevkinite from other localities, along with samples of allanite and keilhauite, were made available for examination through the courtesy of the U. S. National Museum and the Harvard University Geological Museum. These and the Arizona mineral were studied petrographically, spectroscopically and by x-ray in order to determine whether they showed significant relationships. Although all are much alike megascopically, these minerals were readily distinguished microscopically and by rapid spectroscopic analysis for Ti, Al and Ca. The following diagnostic properties serve to distinguish them:

Mineral	Refractive Index	2 V and sign	Ti	Al	Ca
Chevkinite	> 1.85	variable (—)	M*	m**	m
Allanite	1.65 to 1.80	large (—)	—	M	M
Keilhauite	> 1.85	small-medium (+)	M	m-M	M

* M = major constituents.

** m = minor constituents.

A powder diffraction pattern of chevkinite was obtained by H. F. Carl of the Bureau Staff with an automatic recording x-ray diffraction spectrometer. This is the first such pattern reported for this mineral. Patterns

of keilhauite, sphene and allanite obtained with the same instrument are compared with chevkinite in Table 1.

TABLE 1. X-RAY DIFFRACTION PATTERNS OF CHEVKINITE, ALLANITE, KEILHAUITE AND SPHENE

Chevkinite (Arizona)		Allanite (California)		Keilhauite (S.W. Africa)		Sphene (Bancroft, Ont.)	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
4.97	m	3.57	m	4.97	w	4.97	m
4.71	m	3.26	w	3.26	S	3.26	S
3.68	w	2.94	S	3.02	S	3.01	S
3.52	m	2.85	w	2.63	mS	2.62	mS
3.20	S	2.74	mS	2.61	m	2.29	m
3.11	w	2.65	m	2.30	w	2.12	w
3.04	m	2.57	w	2.27	w	2.07	w
2.91	m	2.19	w	2.12	w	1.95	vw
2.77	w	2.14	w	2.08	w	1.81	vw
2.74	S	1.91	w	1.96	w	1.75	vw
2.38	w	1.65	m	1.75	vw	1.71	vw
2.19	w			1.71	w	1.65	m
1.98	m			1.65	m	1.51	w
				1.50	w	1.42	w
				1.42	w		

d = interplanar spacing, in Angstroms

I = relative intensity

S = strong

m = medium

w = weak

X-ray diffraction studies indicate that both chevkinite and allanite may be either amorphous or crystalline. Chevkinite from Arizona gives a diffraction pattern, whereas samples of this same mineral from Virginia and Madagascar do not. Similarly, allanite from California gives a diffraction pattern, whereas allanites from Russia, Madagascar and Virginia available to us give no pattern. Keilhauite from Africa gives a diffraction pattern (Table 1) very similar to that of sphene, of which it is apparently a variety. The amorphous varieties of chevkinite and allanite from Virginia and Madagascar gave no patterns after being heated at temperatures varying between 300° and 600° C. for periods between 1 and 2 hours.

Crystallographic studies by Baldireff (1925) and Bold'irev (1924) on the Russian material indicate that it is monoclinic. Lacroix (1915) and Ungemach (1916) state that the Madagascar material is either monoclinic or orthorhombic, hemimorphic. Eakins (1891) believed the Virginia material to be amorphous. The most recent description of chevkinite (Korea) is very similar to that of the Arizona mineral. Sin Hata (1940) describes the Korean mineral as a crystal whose form is indistinct, color

black and fracture uneven. It has a hardness of 7, a specific gravity of 4.72 and $n > 1.85$. The crystal system of the Korean and the Arizona minerals could not be determined.

CHEMISTRY

Chevkinite is a titano-silicate containing iron, thorium and members of the cerium group of rare-earth metals.

Chemical analyses of chevkinite appear in the literature as early as 1844. Analyses have been reported by H. Rose (1844); M. A. Damour (1861); R. Hermann (1866); R. C. Price (1888); L. G. Eakins (1891); Lacroix (1915); L. E. Kaufmann (1924); I. P. Alimarin (1935) and Sin Hata (1940).

Selection of the sample in this, as in every case, is most important; several of the above investigators state that their samples analyzed were impure mixtures. The sample used in this analysis was carefully prepared. Fragments were examined under a binocular microscope and only those free of noticeable impurities were selected. These grains were ground in a boron carbide mortar to avoid contamination by silica, alumina or iron. Numerous mounts examined microscopically indicated only a trace of impurities.

The chemical composition of the Arizona mineral is compared with published analyses of chevkinite in the following table.

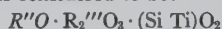
TABLE 2. CHEMICAL COMPOSITION OF CHEVKINITE

	1	2	3	4	5	6	7	8	9	10	11
SiO ₂	12.04	21.04	20.68	19.03	23.28	20.21	21.49	19.23	17.66	18.60	23.73
TiO ₂	17.08	20.17	16.07	20.86	21.16	18.78	18.99	19.61	17.93	19.30	19.55
ThO ₂	0.82	—	20.91	—	—	0.85	0.75	0.73	0.67	0.83	2.61
Ce ₂ O ₃	25.29	—	—	—	11.89	20.05	19.08	20.52	14.21	22.67	33.35
(LaDi) ₂ O ₃	18.35	47.29	22.80	38.38	20.34	19.72	17.16	18.77	24.09	21.83	—
Y ₂ O ₃	1.50	—	3.45	—	—	1.82	1.64	0.93	2.45	—	1.56
Al ₂ O ₃	0.93	—	—	7.72	—	3.60	3.65	2.17	0.23	3.35	0.58
Fe ₂ O ₃	9.56	—	—	—	5.63	1.88	2.89	2.60	8.81	1.91	3.07
FeO	7.76	11.21	9.17	7.96	5.56	6.91	5.92	8.75	9.95	8.20	6.07
MnO	0.50	0.83	0.75	0.38	—	—	—	1.11	tr.	—	2.00
CaO	3.35	3.50	3.25	4.40	5.48	4.05	5.24	2.49	2.12	3.30	2.91
MgO	0.74	0.22	—	0.27	0.64	0.55	0.48	0.05	0.31	0.60	0.12
Cb ₂ O ₅	—	—	—	—	—	0.08	0.08	0.01	0.63	—	—
Cr ₂ O ₃	—	—	—	—	—	—	—	0.07	—	—	—
(NaK) ₂ O	—	0.12	—	—	0.32	0.06	0.04	0.10	—	—	—
SnO ₂	—	—	—	—	—	—	—	—	0.25	—	—
ZrO ₂	—	—	—	—	2.29	tr.	tr.	—	—	—	3.42
BeO	—	—	—	—	2.15	—	—	—	—	—	0.04
UO	N.D.*	—	2.50	—	—	—	—	—	—	—	—
SO ₂	—	—	—	—	—	—	—	0.15	—	—	—
P ₂ O ₅	0.38	—	—	—	—	—	—	—	—	—	—
H ₂ O	1.50	—	0.42	1.30	1.90	0.94	2.06	0.81	—	—	—
	99.80	104.38	100.00	100.30	100.64	99.50	99.47	98.10	99.31	100.59	99.01

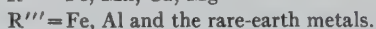
* N.D. = Not detected.

1. Chevkinite—Mohave County, Ariz.
2. Chevkinite—Urals (H. Rose) (1844)
3. Chevkinite—Urals (R. Hermann) (1866)
4. Chevkinite—Southern India (M. A. Damour) (1861)
5. Chevkinite—Nelson County, Va. (R. C. Price) (1888)
6. Chevkinite—Bedford County, Va., I, lustrous material (R. G. Eakins) (1891)
7. Chevkinite—Bedford County, Va., II, dull material (R. G. Eakins) (1891)
8. Chevkinite—Urals (I. P. Alimarin) (1935)
9. Chevkinite—Korea (Sin Hata) (1940)
10. Chevkinite—Madagascar (Lacroix) (1915)
11. Chevkinite—Sabaragamuwa, Ceylon (G. Tschernik) (1913)

The general formula is considered to be:



when:



The formulae calculated from the above analyses are:

Sample	$R''O$	$R_2'''O_3$	$(SiTi)O_2$
(1) Arizona	1	1	2
(2) Urals	2	1	5
(3) Urals	1	1	3
(4) So. India	1	1	3
(5) Nelson Co., Va.	2	1	5
(6) Bedford Co., Va.	1	1	3
(7) Bedford Co., Va.	1	1	3
(8) Urals	1	1	3
(9) Korea	1	1	3
(10) Madagascar	1	1	3
(11) Ceylon	1	1	5

The rare-earth metals are a group of elements, nearly all trivalent, whose compounds have marked similarity. The entire group forms oxalates insoluble in oxalic acid, affording a means of separating the group from most of the other elements. The determination of the rare-earth metals as a group can be accomplished easily and rapidly, but the determination of individual members is more difficult.

The group can be precipitated quantitatively by ammonium hydroxide, which serves to separate it from the alkalis, alkaline earths and magnesium. This ammonium group, however, will also contain aluminum, iron, titanium and any other element that will precipitate under these conditions. This precipitate can be dissolved in hydrochloric acid and the rare earths precipitated from the solution by the addition of oxalic acid. A heavy, white granular precipitate will appear after vigorous stirring. (This procedure may be used to determine qualitatively the presence of the group if a spectroscope is not available.)

The analyst can separate quantitatively thorium, cerium, lanthanum and didymium (praseodymium and neodymium) and the yttrium group from this precipitate.

PETROGRAPHY

Intimately associated with the Arizona chevkinite, in one portion of the sample, are sphene, monazite, apatite, cronstedtite and quartz. Two thin sections were made of the impure portion of the sample to determine the relationship of chevkinite to the associated minerals. The sections contain anhedral chevkinite, which is traversed by irregular cracks and shows no discernible cleavage; numerous euhedral grains of apatite; small euhedral to large anhedral grains of sphene; small subhedral to large euhedral grains of monazite; large, uniformly oriented flakes of cronstedtite; and a small amount of strained quartz. The flaky material, thought to be cronstedtite, always shows the same orientation and is very strongly pleochroic from pale brown to almost opaque. Its lowest refractive index is equal to 1.805. It is biaxial negative with a small axial angle and shows distinct dispersion with $r < v$. Cross, who examined several sections of chevkinite from Virginia for Eakins (1891), describes a similar mineral found replacing chevkinite. He writes, "This mineral is also strongly pleochroic, varying from yellow-brown to chestnut brown. All of it in the sections seems to have a uniform crystallographic orientation, the cause of this uniformity not being apparent." The optical properties of this mineral are similar to those of the high iron chlorite, cronstedtite.

The euhedral character of the monazite, sphene, and apatite, as well as the cross-cutting relationships of these minerals to chevkinite, indicate that they have crystallized after the chevkinite and have been derived, at least in part, from this mineral. The cronstedtite also appears to replace the chevkinite. The rare earths and thorium necessary for the formation of the monazite, the titanium for sphene and the iron for cronstedtite may have been supplied by chevkinite. There is no clue to the source of the phosphate, lime, and additional silica necessary for the formation of monazite, sphene and cronstedtite.

The origin of the chevkinite, in this instance, cannot be definitely established. Its occurrence in a vein associated with a "granite dike" suggests that it was formed in a pegmatitic environment, the host of many of our rare radioactive minerals.

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NOTES AND NEWS

CORRECTIONS TO DANA'S SYSTEM OF MINERALOGY, VOLUME ONE, SEVENTH EDITION

CLIFFORD FRONDEL, *Department of Mineralogy, Harvard
University, Cambridge, Mass.*

The accompanying list details all of the significant corrections that have so far been found in the first printing of volume one of the seventh edition of Dana's System of Mineralogy (John Wiley and Sons, New York, 1944). These corrections, together with others of a minor nature, have been effected in the second printing of the work (January, 1946), and are listed here for the information of holders of the original printing. A few additional corrections, found too late for inclusion in the second printing, are also listed. These are indicated by an asterisk preceding the page number. Reprints of this paper may be obtained from the above address.

<i>Page</i>	<i>Line</i>	
viii	14, up	<i>for years read months.</i>
6	5, down	<i>for structure factors read structural controls.</i>
6	13, up	<i>for The crystal symmetry class notation used here is that of Rogers read The class names used here are those of Groth modified by Rogers, . . .</i>
9	1, down	<i>for in the lower column read in the column headed "lower."</i>
*13	Eqn. 25	<i>for $c = \frac{q_0' \cos \nu \sin \lambda}{\sin \mu}$ read $c = \frac{q_0' \cos \rho_0 \sin \nu}{\sin \mu}$.</i>
14	3, down	<i>delete the brackets around the equation.</i>
14	Table 4	<i>delete the vertical bar between Class and 1 and center the heading Class 1 over the two left-hand columns.</i>
20	Table 5	<i>delete the vertical bar between Class and m and center the heading Class m over the two left-hand columns.</i>
22	Eqn. 69	<i>for $\tan \rho = C$ read $\tan \rho = \tan C$.</i>
*22	6, up	<i>for the angle to $-m(\bar{1}\bar{1}0)$ read the angle to $-m(\bar{1}10)$.</i>
25	8, up	<i>for $i = (h+k)$ read $\bar{i} = (h+k)$.</i>
32	Table 14	<i>for form e under column $\rho = A_3$, for $26^\circ 33'$ read $26^\circ 34'$, and under column A_2 for $63^\circ 27'$ read $63^\circ 26'$.</i>
41	20, up	<i>the sentence beginning The degrees of . . . should be made a new paragraph.</i>
43	Ref. 24, footnote	<i>for 556 read 566.</i>
48	9, down	<i>for 1922 read 1916.</i>
48	14, down	<i>for tables read atlas, and for 1922 read 1916.</i>
62		<i>under Roy. Soc. Edinburgh, Trans. for vol. 1-57, no. 6, 1783-1932 read vol. 1, 1783-date.</i>
64		<i>under Zs. anorg. Chem. for vol. 51-100, 1906-07 read vol. 51-100, 1906-17.</i>
68		<i>under Clarke (1924) for 1934 read 1924.</i>

- 75 *under Kraus, Hunt and Ramsdell (1936) for S. L. Ramsdell read L. S. Ramsdell and for 1836 read 1936.*
- 85 5, up *for Millimicrons = 10^{-6} cm = $\frac{\text{\AA}}{100}$ read Millimicrons = 10^{-7} cm = 10\AA .*
- 87 *under Class 1, Type 2, for Non-metals read Non-metals and semi-metals.*
- 87 *under Class 5, add Type 3, Miscellaneous.*
- 87 *under Class 6, delete Type 3, Miscellaneous.*
- 104 *under Ref. 2, for (Ag₈Hg) read (Ag₈Hg₈).*
- 110 4, down *for planet read planetoid.*
- 112 *under citation of analyses, insert 7. before Borneo⁸.*
- *113 *in Ref. 1, for 3 2/m read $\bar{3}$ 2/m.*
- *113 *in Ref. 3, for 1016 read $10\bar{1}6$ and for 1012 read $10\bar{1}2$.*
- *123 *under Forms, for $\bar{n}\{101\bar{4}\}$ read $\bar{n}\{10\bar{1}4\}$.*
- 128 *under Arsenic, Cryst., for 3 2/m read $\bar{3}$ 2/m.*
- 128 *under Forms, for Z 0118 read \bar{z} 0118, and for P 0112 read \bar{p} 0112.*
- *132 *under Forms, for c 001 read \bar{c} 0001.*
- *136 *under Forms, for m 1010 read \bar{m} 1010.*
- 140 *under Sulfur, Cryst., read $q_1:r_1:p_1$ in the ratio $q:r:p=0.8131:0.4272:1$, and read $r_2:p_2:q_2$ in the ratio $r:p:q=0.5254:1.2298:1$.*
- 146 11, down *for hydrosulfate read hydrosulfide.*
- 147 *In the two figures on the right in the top row, for c read a.*
- 151 Ref. 5 *for 7 read 360.*
- 151 Ref. 15 *for Hey read Bannister and Lonsdale.*
- 152 bottom line *for 1.93-207 read 1.93-2.07.*
- 154 Ref. 1 *for 27 read 26.*
- 160 *under Structure cell, add Space group $R\bar{3}m$.*
- 162 *under Structure cell, for Space group $R\bar{3}$, $R32$ or $R\bar{3}m$ read Space group $R\bar{3}m$.*
- 163 6 and 7, up *for Temiskaming district read Cochrane district.*
- 165 *to Ref. 4, under oruette, add See also Peacock (Univ. Toronto Stud., Geol. Ser., 46, 83, 1941).*
- 168 *in Anal. 1, for 10.33 read 10.01, for 0.32 read 0.60, and for total, 100.08, read 100.04.*
- 169 1, top *for Rem. is Fe 0.32 read Rem. is Fe 0.32, SiO₂ 0.28.*
- 175 *under Anal., for Fe₂O₃ read Fe₂O₃.*
- 177 *in figure, for c read a.*
- 184 3, up *for Hg₂Te read Ag₂Te.*
- 192 *in last line of Ref. 2, for 29 read 28.*
- 198 *under Opt., delete $n_D=1.6654$.*
- *210 *under Forms, for $-\beta$ 223 read $-\beta$ 223; for γ 225 read $-\gamma$ 225; for Z 357 read $-\bar{Z}$ 357.*
- 215 *under Forms, for q 112 read n 112, and for $-q$ 112 read $-\bar{n}$ 112.*
- 216 *in figure, for k read n.*
- *220 *under Forms, for $-\bar{p}$ 112 read $-\bar{p}$ 112.*
- 225 *in right hand figure, transpose $-\bar{p}$ and $-\bar{n}$.*
- *229 *under Forms, for γ 7078 read γ 7078.*
- 231 *in Niccolite Group tabulation, after 2656 Pentlandite for (Fe, Ni)S read (Fe, Ni)₈S₈.*

- 234 under *Artif.*, for FeS read FeS₂.
- 235 12, down for (3×3.433) read $(\sqrt{3} \times 3.433)$.
- *240 under *Forms*, for $-\mu$ 1453 read μ 1453.
- *249 under *Less common forms*, for g $3 \cdot 0 \cdot 3 \cdot 16$ read g $3 \cdot 0 \cdot \bar{3} \cdot 16$.
- *252 under *Forms*, for i 2025 read i 2025; for Δ 1012 read Δ 1012; for $-q$ 0221 read $-q$ 02 $\bar{2}$ 1; for u : ' 1124 read u : ' 11 $\bar{2}$ 4.
- *253 7, up for Idrilin read Idrialin.
- *255 5, down under *Uncertain forms*, for $1 \cdot 0 \cdot 1 \cdot 14$ read $1 \cdot 0 \cdot \bar{1} \cdot 14$.
- *260 6, down in Ref. 2, for space group *Pnma* read space group *Pm \bar{c} n*.
- 270 under *Forms*, for ϕ 120 read o 120.
- 274 under *Artif.*, for Sb₂O₂ read Sb₂O₃.
- 278 bottom line for bismutosphalerite read bismutosphaerite (or, more correctly, bismutite).
- 279 under *Kermesite*, *Cryst.*, insert superscript 2 after axial ratio, i.e., $a:b:c=1.339:1:1.265^2$.
- 283 in right hand figure in the middle row (Urals) for e' read ' e '. Note also in the second figure in the top row that the striations on the cube face (010) should be horizontal.
- 292 after *Artif.* add Name. Named by Wöhler as a compliment to the wife of a personal friend.
- 294 in line 9 under *Occur.* for Wakatipu district, Collingwood, New Zealand read Wakatipu district, and Collingwood, New Zealand.
- 303 line 8 in synonymy after *Loellingite*, for Pharmakopyrit read Pharmakopyrit.
- 304 in bottom right hand figure, from Center Strafford, N. H., add caption (Old orientation; $z=s$, $l=m$, $m=e$).
- *307 in *Structure Cell*, for Co₄As₈⁴ read Co₄As₈¹¹.
- *309 under ref. 10 add 11. de Jong (*Physica*, **6**, 325, 1926) by powder and rotation methods on material from Schneeberg.
- 309 delete analysis no. 3 and the corresponding citation (Hudson Bay mine).
- 310 in Ref. 4, line 2, for 670 read 676.
- 318 in the middle figure of the top row, for the caption Serbia read Serbia. $\alpha\{1.24.0\}$.
- 326 under *Chem.*, add superscript 2 as follows: Only one analysis has been made.²
- *333 under *Krennerite*, *Cryst.*, for Orthorhombic; dipyrarnidal—2/ m 2/ m 2/ m read Orthorhombic; pyramidal— m m 2.
- *338 under *Sylvanite*, *Forms*, for N $\bar{1}03$ under ϕ for $-90^\circ 00'$ read $90^\circ 00'$; and in list of less common forms for X $\bar{3}11$ read K $\bar{3}11$.
- 340 17, down for Kirkland Lake read Porcupine.
- 343 in *Anal.* no. 4, for 75.30 read 75.70 and for total, 99.54, read 99.94.
- 344 in analysis citation no. 16, for Cobalt, Ontario read Oravicza, Roumania.
- 344 in analysis no. 24, for 74.54 read 74.52, and for total, 99.74, read 99.72.
- 345 23, down for Goat Hill read Great Hill.
- 346 in Ref. 23, for 80 read 81.
- 348 after 3313 *Colusite*, for Cu₃(Sn,Te,V,As)S₄ read Cu₃(Sn,Te,Fe,V,As)S₄.
- 348 after 31. *A_mB_nX_p* Type, for $m+n>4:3$ read $m+n:p>4:3$.

- 351 *in right hand figure, for the lower face p read P, for the lower face r read R, and for the lower face-labeled n read N.*
- 352 *in citation of analysis no. 3, for Quespisiza, Chile, read Quespisiza, Peru.*
- 354 *in the figure, transpose p and r on the upper faces, and label the bottom face in the same zone R and the face next above P.*
- 359 *in list of less common forms, for l 233 read l 223.*
- *369 *under Forms, for P 141 read P I41.*
- 371 *under Forms, for P 111 read P I11.*
- 373 *for Occur. read Occur.⁷*
- 376, 377, 378 *under Anal., for ferrian read ferroan in the captions to anal. 5, 6, 8, 14, 18, 28, 30, 34.*
- 378 *in the citation to analysis no. 29, for (and bismuthian) read (and bismuthian, ferroan). In the citation to analysis no. 35 for (sandbergite) read (sandbergerite).*
- 390 *in the right hand figure, for f read II.*
- 395 *transpose the right hand figure with the lower right hand figure (Harz) on page 407.*
- 407 *in the lower left hand figure, for n read η .*
- *417 top line *for c_0 6.88 read c_0 5.88.*
- 417 *in the left hand figure, transpose w and v.*
- 440 *under Forms, in the column headings to the angle table for ρ read $\rho = C$; for ρ_1 read $\rho_1 = A$; for ρ_2 read $\rho_2 = B$.*
- *440 *in Structure cell, for Space group Pnma read Space group Pmcn.*
- 440 *in the caption to analysis no. 3, for SnS read ZnS.*
- 443 *in the figure, for x read v, and for the prism forms F K m s read s m K F.*
- *443 *under Forms, for form π I11 under column ϕ , for $6^\circ 40'$ read $-6^\circ 40'$.*
- 450 *in line 2 in Ref. 1, for to new elements read to new elements in the preferred position.*
- 458 *in the figure labeled San Jose, Bolivia, for the brachydome v read π .*
- 461 11, down *insert superscript 5 after formula, e.g., $Pb_4As_6S_{13}^5$.*
- 465 top line *for 5.533 read 5.60.*
- 469 *in figure, for u read U, and for v read v.*
- 471 *under Forms, for G 211 read g 211, and in the list of less common forms, for g 311 read G 311.*
- 472 3, down *for A bismuth sulfide, read A lead, bismuth sulfide.*
- 484 *in the right hand figure, for σ read o.*
- 491 *in the tabulation of the AX_2 Type, in line 14 for 4581 Bismite read 447 Bismite, and for 4582 Sillenite read 448 Sillenite. (These species properly belong at the end of the AX_3 type.)*
- 491 *Following Sillenite, insert a heading 46. A_mX_n Type, and change the type numbers under it as follows: for 459 Vanoxite read 461 Vanoxite, for 45.10 Corvusite read 462 Corvusite, for 45.11 Ilsemannite read 463 Ilsemannite, for 45.12 Russellite read 464 Russellite, for 45.13 Tungstite read 465 Tungstite.*
- 492 *in the upper left hand figure, labeled Wheal Phoenix, Cornwall, for x read F.*
- 494 *in Ref. 1, line 3, for (155, 1916) read (155, 1915).*
- *495 *under Forms, for y Okil read y Okil*

- *504 under Forms, for α 4045 read α 4045.
 *505 in caption under figure, for $f\{20\bar{2}1\}$ read $f\{11\bar{2}2\}$.
 *508 under Forms, for form $\{101\}$ read $\{\bar{1}01\}$.
 518 2, down in analysis no. 1, for Pb_3O_4 9.39 read 91.39.
 *528 under Forms, for μ 0115 read μ 0115, and for s 0221 read z 0221;
 in the list of less common forms for λ 10.1.16 read λ 1.0.1.16, and for
 z 2241 read s 2241.
 *535 under Ilmenite forms, for P 0551 read P 0551.
 537 in citation of analyses, after no. 1, for $FeTiO_2$ read $FeTiO_3$.
 544 bottom line for calamine read cerussite.
 546 in the right hand figure, for u read a .
 550 at the top of the page, in the third column of forms, for 5.3.0 read 530,
 and in the fifth column, for 0.11. read 0.11.8.
 555 under Forms, for z 231 read Z 231.
 563 in the fifth line under Chem., for ebelmanite read ebelmenite
 566 in line 7 under the heading Wad, delete (and cryptomelane)
 *567 under Anal., insert 7 at top of the right hand column.
 570 16, down for Sweden read Norway.
 15, down for Black Forest read Odenwald.
 14, down for Rhine Province read Westphalia.
 16, down for in the Tirol read, Salzburg.
 577 19, up for Wyoming read Nevada.
 579 5, down delete Near Burns, Oregon.
 8, down for Wyoming read Nevada.
 10, down for pageite read paigeite.
 12, down for Algoma district read Sudbury District.
 584 in the left hand figure in the top row, for η read n .
 598 10, down for Ontario read Quebec.
 599 for 4581 Bismite read 447 Bismite.
 601 for 4582 Sillenite read 448 Sillenite.
 601 for 459 Vanoxite read 461 Vanoxite.
 602 for 45.10 Corvusite read 462 Corvusite.
 603 2, up for $MoO_3SO_3 \cdot 5H_2O$ read $MoO_3 \cdot SO_3 \cdot 5H_2O$.
 *604 7, up for $\bar{4} 2/m$ read $\bar{4} 2 m$.
 604 for 45.12 Russellite read 464 Russellite.
 605 for 45.13 Tungstite read 465 Tungstite.
 607 in the tabulation of oxides containing uranium, for 531 Becquerelite
 read 523 Becquerelite, for 532 Schoepite read 524 Schoepite, for 533
 Fourmarierite read 531 Fourmarierite, for 534 Curite read 532 Curite,
 for 535 Uranosphaerite read 533 Uranosphaerite, for 536 Vandenbrandite
 read 534 Vandenbrandite, and for 537 Ianthinite read 535 Ianthinite.
 608 under Forms, for r 102 read r 102.
 608 in the figure, for n read y , and in the caption to the figure for Rak-
 wana, Ceylon, read Balangoda, Ceylon.
 625 for 531 Becquerelite read 523 Becquerelite.
 627 for 532 Schoepite read 524 Schoepite.
 628 for 533 Fourmarierite read 531 Fourmarierite.
 629 for 534 Curite read 532 Curite.
 631 for 535 Uranosphaerite read 533 Uranosphaerite.
 632 for 536 Vandenbrandite read 534 Vandenbrandite.

- 633 for 537 Ianthinite read 535 Ianthinite.
 635 in tabulation of AX_3 Type, bottom line, for 625 Psilomelane read 618 Psilomelane (belongs in AX_2 type).
 646 in Ref. 5, for 0.20 read 0.020.
 656 6, down for Tasmania read Transvaal.
 658 2, up for Sweden read Norway.
 665 5, up for chalcocaluminite read chalcocalumite.
 668 in citation no. 1 under the analyses, for $Ca_4Al_6(OH)_{14} \cdot 5H_2O$ read $Ca_4Al_2(OH)_{14} \cdot 5H_2O$.
 668 for 625 Psilomelane read 618 Psilomelane.
 673 bottom line in the formula for 762 Zirkelite, for $(Ca, Fe, Th, U)(Ti, Zr)_2O_6$ read $(Ca, Fe, Th, U)_2(Ti, Zr)_2O_6$.
 691 5, up for SnO_2 read SiO_2 .
 *706 in ref. 12, for (001) pyrophanite read (0001) pyrophanite.
 707 11, up for Vredenbergite read Vredenburgite, and for 199 read 42.
 721 10, down for Porte read Poste.
 721 3, up for 17 read 9.
 *724 in angle table, for $d \bar{1}01$ under ϕ , for $90^\circ 00'$ read $-90^\circ 00'$.
 *726 under Less common forms, for q 2023 read q 2023.
 742 top line for Hf read HF.
 746, 747 for the caption $A_mB_nX_x$ Type read $A_mB_nX_p$ Type.
 764 under Anal. for La_2O read La_2O_3 .
 771 in caption to analysis no. 1, for Al_2Ta_2O read $Al_2Ta_2O_8$.
 772 4, up for Ca_2O_3 read Ce_2O_3 .
 779 under Chem., line 2, for $(A_2B_3B_{10})$ read $(A_2B_3O_{10})$.
 782 the formula given for the specific gravity of members of the columbite-tantalite series, beginning on line 7, should read $(5.20 + 0.03 \times \%Ta_2O_5 = G \pm 0.05$ for . . .)
 *792 4, up for Eschwegite read Eschwegeite.
 797 in the figure, for d read e , and for e read x .
 801 the caption for analysis no. 2 should read 2. Plumboniobite. Rem. is loss on ign.
 809 Ampangabeite, for 805 read 806.
 811 Baddeleyite, for 607 read 607, 608.
 813 for Cacheutite read Cacheutaite.
 814 for Colbaltpyrite read Cobaltpyrite.
 814 for Colbaltum . . . read Cobaltum . . .
 *816 for Eschwegite read Eschwegeite.
 819 Hydroeuxenite, for 805 read 806.
 820 Jacut, for 420 read 520.
 820 Kayserite, for 679 read 680.
 821 Kochelite, for 762 read 757, 762.
 822 Magnetoplumbite, for 727 read 728.
 824 Nematite, nematolite, for 637 read 636, 638.
 824 Nigrin, for 558 read 555, 558.
 827 for Rammelsbergit read Rammelsbergite.
 828 Schirmerite, for 423 read 424.
 831 Tanatarite, for 679 read 680.
 833 for Vredenbergite read Vredenburgite.
 833 Vanadic Acid; Vanadic Ocher, for 493 read 494.

GERMAN MINERALOGISTS AND GEOLOGISTS

R. G. WAYLAND, *U. S. Geological Survey, Washington, D. C.*

During a recent tour of duty with the Military Government in Berlin, the writer had occasion to have a number of visits with German mineralogists and geologists remaining in the city. One of the by-products of these visits was a set of notes representing the best available information on the present location and status of German mineralogists and geologists from nearly all of the leading German universities and mineralogical laboratories. Professor Paul Ramdohr of the Mineralogy-Petrology Institute, University of Berlin, was the principal source of the notes. Neither he nor the other German mineralogists visited claim their news to be complete, entirely accurate, or current. However, American mineralogists may be interested in learning something of the whereabouts of Germans with whom they may have had professional contact or personal acquaintance, even though some of the news is little better than gossip. It must be appreciated that the German postal system is even yet entirely inadequate to permit normal intercity correspondence and that the long-distance telephone is still a thing of the past for 99 per cent of the German population. Indeed the writer considers it remarkable that contacts have been established and news passed along to the extent that these notes indicate.

As a generalization, Germany has comparatively few younger mineralogists to replace those dead, retired or "inactivated" as a result of Nazi party membership. Many of those men who were professors before the Nazis came into power succeeded in holding their positions without joining the party, but younger aspirants found in general that they would have to become party members if they were to become professors. If they did so, they cannot be employed as educators and in professional positions now under Military Government, and if they did not, they generally left the field and entered industry or went into military service from which many of them have not returned.

If it is shown later that any of the following statements are both inaccurate and damaging, particularly any that brand a man as having belonged to the Nazi party, it is deeply regretted by the writer. On the other hand other men mentioned may well have had party membership without the writer hearing of it.

Professor Walter Schmidt of the Berlin Technical High School died during the Battle of Berlin in May 1945 on active duty with the Volksturm. Professor Bernauer, his assistant, died then, likewise, from infection in an arm wound suffered from a bomb fragment. Bernauer lived for fourteen days without food and medical care after he was struck. He was

known for his volcanology and hot springs studies, while Schmidt was known for his work on the metamorphics and petrofabrics.

Professor Belowsky died August 1945 in Berlin in an automobile accident a few days before his 80th birthday. He had bad hearing and did not notice the approach of an American military vehicle. Professor Von Zur Mühlen is living in Berlin but is no longer connected with the Technical High School because he was a Nazi party member. The Technical High School building itself is in utter ruin. The buildings housing the Prussian Geological Survey and the Mineralogy-Petrology Institute on Invalidenstrasse are damaged, but largely in use. The Kaiser Wilhelm Silicate Research Laboratories are also damaged but in use. Professor Wilhelm Eitel, the former director, was removed as a Nazi party member, but like many others so affected by Military Government law No. 8, he has appealed and his future status is uncertain. Professor Hans Stille of the University of Berlin, well known for his book on the structural geology of the Americas and other works, is in good health, as is Mrs. Stille.

Professor Schneiderhöhn remains at Freiburg and is well. The institute there was mostly destroyed but it has a new roof now and Schneiderhöhn can work a little. Professor Erdmannsdorfer is still at Heidelberg and is well, though aging. The Heidelberg institute was undamaged. Professor Steinmetz is well in Munich, but the institute there is destroyed. The institute in Frankfurt was also destroyed and Professor Nacken has gone to Tübingen where the institute was not damaged. Professor Weigel of Marburg died of cancer and has been succeeded by a metallographer; the Marburg institute is in good condition. At Giessen the institute was destroyed, and Professor Lehmann is well but inactive; Professor Hummel committed suicide in May 1945. The institute at Erlangen is undamaged but Professor Christa has retired and his successor has not yet been chosen.

Professor Chudoba at Bonn was a Nazi and has been detained. Professor Hans Cloos remains at Bonn and is well, but the institute is half destroyed. Professor Philipp of Cologne and his wife died when a train on which they were riding was strafed by aircraft. Professor Ehrenberg at Aachen is detained in Hanover as a Nazi, and Professor Dannenberg died in March 1946 at 80, to be succeeded by Professor Rohde. The Aachen institute is half destroyed—the mineral collection is undamaged, but the ores are gone. Professor Beger of Hanover, known especially for his post-mortem silicosis mineralogy, is well and is recognized as an anti-Nazi, but the Hanover institute is destroyed. Professor Correns is well and remains at Goettingen where the institute was not damaged, but Professor Schriel of that institute was a Nazi party member. The institute

in Hamburg is in good condition in the center of devastation and Professor Rose remains there, but was a Nazi; Professor Brinkmann has gone to Halle. At Kiel the institute was largely destroyed; Professor Gripp remains, but Professor Leonhardt was a Nazi party member and his status is not known to the writer.

In the Russian Zone of Occupation, the institutes at Leipzig and Dresden were completely destroyed. Professor Scheumann of Leipzig has gone to Bonn to replace Chudoba. Professors Schiebold and Heinz of Leipzig were both Nazi party members and their present status is not known to the writer. Professor Rimann of Dresden died of cancer in 1944 and his successor has not yet been appointed. Professor Tröger, Dresden petrographer, was a Nazi party member and is at present a laborer in the Bavarian forests. At Jena the institute is undamaged; Professor Linck is well at 90 but has retired and has been succeeded by Professor Heide, meteorite specialist released from the Wehrmacht. Professor Seifert has left Jena for Munster where the institute is partly destroyed. The institute at Halle is undamaged and Professor Von Wolfe, the volcanologist, remains, but Professor Weigelt, the vertebrate paleontologist well known in the United States, was a friend of Herman Goering and is now in Goettingen working as a receptionist.

From the parts of Germany now incorporated in Poland, Professor Schlossmacher of Königsberg has gone to Freiberg but is not connected with the Freiberg institute. Professor Spangenberg of Breslau, known especially for studies on crystal growth and on nickel silicates and serpentine minerals, is now in Jena, and Professor Bederke of Breslau has gone to Goettingen to succeed Schriel.

In Austria Professor Sander is well and the institute at Innsbruck is not badly damaged by the medium bomb that fell near it. Professor Machatschki is now at the Vienna institute working on silicate structures. Professor Angel of Graz, known especially for Alpine minerals, textures and metamorphism, is in an Austrian prison and may have been succeeded by Professor Heritsch.

ADDENDA

The following additional information is from a report in *Nature*, May 11, 1946, on "The present state of some German museums" by F. J. Griffin.

J. Wanner, N. Tillman, E. Jaworski and W. Berthier are reported safe at Bonn. W. Kleber and C. Troll are reported well.

Herman Schmidt and Dr. Kremp are on the staff at Goettingen. Dr. Thienhaus was a Nazi and has been dismissed. Dr. W. von Engelhardt was a Nazi and is a prisoner.

AN OCCURRENCE OF WAPPLERITE IN NEVADA

HATFIELD GOUDEY, *Yerington, Nevada.*

A single boulder recently collected from the dump of the White Caps mine, near Manhattan, Nevada, shows very thin white seams of a snow-white mineral on both realgar and orpiment in a gray limestone. The white mineral exhibits no crystalline structure macroscopically and was suspected of being some hydrous calcium arsenate, other than the fibrous pharmacolite frequently encountered in the White Caps ore.

Microchemical tests showed the mineral to be essentially a calcium arsenate with apparently no other elements present.

Under the microscope a finely crystalline structure could be observed. Very rarely straight line edges were found on some fragments and these showed an inclined extinction with a fairly large angle. By immersion in oils the mean refractive index was determined to be about 1.55. In Larsen and Berman's Tables (*U. S. Geol. Sur., Bull.* 848) the optical data for wapplerite is incomplete but the mineral is listed with a mean index near 1.55. Since no other simple calcium arsenate has similar refractive indices it seems likely that the mineral here described should be classified as wapplerite.

Doubtless the calcium arsenate in this occurrence is derived from the alteration of calcite and arsenic sulfides. There is some suggestion that the calcium arsenate as first formed may have been entirely pharmacolite, as occasionally a crudely fibrous appearance is observed in the wapplerite. Rare minute fibers were observed on the specimens derived from the boulder and while they could not be readily isolated for optical tests, they are assumed to be probably pharmacolite. Since wapplerite could be formed from pharmacolite by a simple process of hydration, its replacement of that mineral in this occurrence is not unlikely. Haidingerite might be expected as an intermediate stage but its presence was not noted on these specimens.

THE BRANCHVILLE, CONNECTICUT, PEGMATITE: A CORRECTION
IN TERMINOLOGYVINCENT E. SHAININ, *U. S. Geological Survey, Washington, D. C.*

In a paper by the writer on the pegmatite at Branchville, Connecticut (*Am. Mineral.*, 31, nos. 7 and 8, 329-345, 1946) there are a few inconsistencies in the terminology of structural units in the pegmatite. After the paper was written, the terminology employed by the United States

Geological Survey was revised and the manuscript was changed accordingly. A few of the changes needed, however, were not made.

There is a distinction between the terms "unit" and "zone" that is not entirely clear in the paper as it appeared. A unit is any part of a pegmatite that is distinct from other parts owing to different texture or mineralogy, or both. Zones are a special kind of unit; they are successive concentric shells with boundaries roughly parallel to the walls of the pegmatite. Furthermore, they appear to be primary; i.e., not formed by replacement of pre-existing units of the pegmatite. Under this classification only the following units in the Branchville pegmatite are zones: border zone, muscovite-quartz zone, microcline-perthite zone, and quartz core. The cleavelandite-quartz, cleavelandite, and cleavelandite-spodumene bodies are units of replacement origin, and therefore should not have been labelled "zones" in the illustrations of the paper.

Corrections that should be made in the text are:

Page 336, line 3: "both zones" should read "both units."

Page 336, line 7: "in the zone" should read "in the unit."

Page 337, line 15: "cleavelandite-quartz zone" should read "cleavelandite-quartz unit."

A NEW OCCURRENCE OF ADAMITE

DAN E. MAYERS AND FRANCIS A. WISE, *Tucson, Arizona.*

During a recent visit to the Ojuella Mine, Mapimi, Durango, Mexico, —a mine famous for the extent of its workings and the uniqueness of its mineralogy—a small pocket of *adamite* was encountered, notable both because it has not previously been described from this locality and for the splendor of its crystallization.

The adamite occurs in radiating form, on a matrix of limonite and calcite, as shiny transparent, greenish-yellow crystals up to 5/16" in length. Elongation parallel to the *b* axis is pronounced and only two crystal forms are prominent: a long macrodome {201}, truncated by a prism {310}.

An article is now in preparation dealing in greater detail with recent observations at this locality.

The Department of Conservation, State of New Jersey, has recently issued Bulletin 59, Geologic Series, Bibliography and Index of the Geology of New Jersey. In this bibliography, prepared by Miss Agnes Grametbaur, are listed books, bulletins, journals, articles, papers and reports on the geology of New Jersey that have appeared from 1753 to July 1, 1945.

The Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C., now has for distribution at a price of ten cents, an excellent small booklet entitled *Geology as a Profession*, Vocational Booklet No. 1, which is prepared by the National Roster of Scientific and Specialized Personnel. The author is Miss Ann R. Taylor working under the direction of Dr. W. T. Read, Chief of the Research Section, with the advice and assistance of many geologists. This booklet describes in about 20 pages the profession of geologist (not including geophysicist). It gives the subdivisions of the geological profession, the working conditions and types of employment, the opportunities for women, the related fields of employment, beginning jobs, advancement and conditions of employment, post-war outlook in the profession, and the qualifications and training, and makes suggestions as to how to get a start. The booklet is attractively illustrated. It would be of special value to advisers of young students, and while written primarily from the employment point of view, would also give those entering the profession a condensed and business-like summary of what they might expect.

R. M. Wilke, well-known mineral collector and dealer of Palo Alto, California, died on Sept. 16, in his eighty-fifth year.

PROCEEDINGS OF SOCIETIES

THE 130th ANNIVERSARY OF THE RUSSIAN MINERALOGICAL SOCIETY

D. P. GRIGORIEV, *Mineralogical Laboratory, Mining Institute, Leningrad, U.S.S.R.*

On January 19, 1947, the Russian Mineralogical Society, the oldest of the existing mineralogical societies in the world, will celebrate its 130th anniversary.

The Russian Mineralogical Society was founded at the very beginning of 1817. In Russia that was the time of the growing interest in minerals and ores. The XVIII century witnessed the discovery of many famous Ural and Siberian mineral deposits whose specimens may be seen in the largest mineralogical museums. In Petersburg and Moscow, in both state and private museums, may be found excellent mineralogical collections from Russia; also in western Europe and North America.

As early as 1815 there was formed a group of naturalists who devoted their leisure time to the study of minerals and exchanged their ideas concerning the geology and mineralogy of Russia. The Mineralogical Society originated with the above group. On January 19, 1817, 33 members of the group adopted the constitution of the new Society, thus laying the foundation for its official existence. L. J. PANSNER, Doctor of philosophy, astronomy and mineralogy, and Professor at the Pedagogical Institute and at the University of Petersburg, was elected the first President of the Society.

The newly formed Mineralogical Society thus came into existence and from the very beginning enlisted eminent Russian and foreign scientists. BEAUMONT, BERZELIUS, DANA, DAUBREE, HALL, HUMBOLDT, LYELL, MURCHISON, ROSE, VERNEUIL, and others were affiliated with the Petersburg Mineralogical Society.

During the first decennary its members succeeded in amassing considerable data on the mineralogy and geology of Russia.

By the time of its 50th anniversary the Mineralogical Society had been widely recognized in the scientific world. To commemorate the 50th anniversary there was published a special volume, "Memoires of the Russian Mineralogical Society," which contained a number of historical papers (Series 2, v. II, 1867), and a comprehensive "Symposium devoted to the 50th anniversary." The jubilee celebration is described in the *Memoires of the Russian Mineralogical Society*, vol. III, pp. 303-410, 1868.

The activity of the Society became especially fruitful in the years that followed. During that flourishing period we find the names of N. J. KOKSHAROV, P. V. EREMEYEV, F. N. CHERNYSHEV and A. P. KARPINSKY—the Presidents and Secretaries of the Society.

Extensive mineralogical and geological investigations carried on throughout the vast areas of Russia, were the results of the society's activity during this period.

In the succeeding years the Mineralogical Society sent its members to numerous places to prepare geological maps, investigate ore deposits and collect samples for mineralogical study. The expeditions of the Society embraced the entire Russian territory, from the shores of the Baltic Sea to Turkestan and to the north-eastern extremities of Siberia. The preparation of the general geologic map of Russia was initiated by the members of the Society.

On January 19, 1917, the Russian Mineralogical Society celebrated its 100th anniversary. Because of war-time conditions it was not possible to carry out the full program of the jubilee celebration. The monumental summarizing work on the progress of petrography in Russia by F. U. LEVENSON-LESSING and the history of the geologic investigations of Siberia by V. A. OBRUCHEV, written specially for the jubilee, were published considerably

later. A. P. GUERASIMOV's paper "The 100th Anniversary of the mineralogical Society" was devoted to the jubilee and was published in the "*Geological Herald*," vol. III, pp. 9-27, 1917.

The 125th anniversary on January 19, 1942, coincided again with the war. In besieged Leningrad under the fire of German high-calibre guns there was held a modest jubilee meeting attended by the members of the Society. The jubilee address delivered by D. P. GRIGORIEV, the secretary of the Society, is published in "Memoires of the Russian Mineralogical Society," vol. LXXI, No. 1-2, pp. 1-8.

After the victorious end of World War II the Russian Mineralogical Society is going to celebrate its 130th anniversary on January 19, 1947.

Numerous investigations were carried out by the Society during the 130 years of its existence. These are represented by the publications of the Society.

The first volume of its publications appeared in 1830 under the title of "*Transactions*"; the second volume was published in 1842. The activity of the Society increased greatly since that time. In addition to the annual publication of "*Transactions*," 27 volumes of "Materials on the Geology of Russia" were published within the period from 1863 to 1916. The "*Memoires*" of the Russian Mineralogical Society have been issued since 1866.* Its 75th volume makes its appearance in 1946. There are four annual numbers of the Memoirs aggregating from 600 to 800 pages. Besides this the Society has published scores of books and other publications.

All told the Mineralogical Society has published more than 120 volumes that contain important data on the mineralogy, geology and ore deposits of the U.S.S.R., as well as of foreign countries such as the U.S.A., England, Africa, India, Germany, Iran, Ireland, Italy, New Caledonia, China, Manchuria, Scandinavia, Ceylon, Japan, and others.

After the recent war the work of the Russian Mineralogical Society is again in full progress. Besides the usual meetings of the members and the annual meeting on January 19, "Fedorov sessions" are held in memory of E. S. FEDOROV, the greatest of all Russian crystallographers. Every year the Society awards an honorary testimonial for the most outstanding work on geology and mineralogy. The Society possesses a large library containing valuable collections of rare editions of the XVIII and early XIX centuries.

In conclusion of this brief review we shall cite the words of S. S. KUTORGA who was the President of the Society in 1845: "It is not ambition that makes us recall all our achievements but the wish to contemplate the excellent future of our Society and to support each other for the advancement of Science!"

* Written in Russian but each article contained an English, German, or French summary.

BOOK REVIEWS

MINERALS OF THE MONTMORILLONITE GROUP. THEIR ORIGIN AND RELATIONS TO SOILS AND CLAYS. By CLARENCE S. ROSS AND STERLING B. HENDRICKS, U. S. Geological Survey, *Professional Paper 205-B.*, 1945.

Few publications of the U. S. Geological Survey can have been more eagerly awaited by fellow workers than the paper under review. It is now twenty years since the data on the montmorillonite clays were assembled and critically examined, in the classic and much quoted paper by Ross and Shannon (*Trans. Am. Cer. Soc.*, 9, p. 77, 1926). In these twenty years much has happened. The clays have advanced from being a confused and neglected family in the vast concourse of minerals to a stable and indeed eminent position, supported by coherent data and splendidly accoutred with fascinating properties. To this improvement the authors and their associates have greatly contributed. By 1931 Ross and Kerr had rehabilitated the kaolin minerals. (*U. S. Geol. Sur. Prof. Paper 165-E*); by 1934, halloysite and allophane also (*U. S. Geol. Sur. Prof. Paper 185-G*). Since then Ross, Hendricks and other associates have concerned themselves chiefly with the montmorillonite group—elusive in constitution, unique in properties. Their methods have been diverse; x-ray, thermal and base exchange studies have been added to the central core of the 1926 work. This consisted of accurate chemical analyses and precise optical constants and has now been very greatly expanded. The results are discussed in the light of contributions from other sources dealing with the planar lattice structure of montmorillonite and its unique characteristic, a variable spacing which increases or decreases according to the pressure of water vapor in its neighborhood. The relationship of base exchange to departures from the idealized composition is strongly emphasized throughout. It is naturally extremely gratifying to the reviewer to find that the deductions he made in 1935 regarding the relationship of the exchange ions to substitutions in the idealized lattice, are so strongly supported.

One of the most pleasing features of this work is the breadth of the mineralogical treatment of the analytical data and the clear demonstration that in the seventy-odd samples on which the main conclusions are based, impurities can have played only a negligible role. The boggy of contamination, which appeared to a recent contributor to this journal [W. P. Kelley, Calculating formulas for fine grained minerals on the basis of chemical analysis' *Am. Mineral.*, 30, 1 (1945)] as effectively barring the way to any detailed interpretation of clay analyses, is now seen reduced to its proper size.

The montmorillonite clays, as is now well-known, are structurally similar to pyrophyllite and talc on the one hand and to the micas on the other. What gives them their unique property of one-dimensional expansion is the fact that the negative charge per lattice unit induced by substitutions, falls in an intermediate range. The cations balancing this charge are less numerous than in the case of the micas; hence their cementing action is correspondingly weaker. Dipoles such as water molecules orient themselves around the cations and force the silicate units apart. One important result of the work under review is that fairly definite limits are set to the magnitude of the charge. It varies from 0.5 to 0.8 equivalents per lattice unit of 24 oxygen atoms, with many samples very close to 0.66. Muscovite mica has a corresponding charge of 2.0 equivalents.

The montmorillonite group as a whole is subdivided by the authors into two series. In each are examples of charges arising in two ways; firstly, by the substitution of Al for Si in the silica sheets; secondly, by that of a divalent for a trivalent ion in the alumina sheet or a monovalent for a divalent in a magnesia sheet. The two series differ in the number of atoms in the middle gibbsite-brucite layer. In the montmorillonite-beidellite-nontronite

series it varies from 4 to 4.4 atoms per unit of 24 oxygens atoms; in the saponite-hectorite series it is relatively constant at 6 atoms. The two are thus well separated.

The predominant replacements are as follows: Al for Si in the beidellites, Mg for Al in the montmorillonites, ferric iron for Al in the nontronites. The charge on the latter is most frequently caused by Al for Si, those with the highest replacement being termed aluminian nontronites. Chromium-containing nontronites (volchonskoite) are also known. It should be noted also that a very high charge in the Si layer is generally partially neutralized by a positive charge in the Al layer. In this way the variation in total charge is kept within the narrow limits mentioned above. In the saponite-hectorite series the saponites have a strong replacement of Al for Si. Hectorite shows the unusual replacement of Li for Mg accompanied also by fluorine proxying for hydroxyl. It may be mentioned in passing that while this paper has been in press a new saponite mineral has been described, in which the Mg of the brucite layer is substituted by Zn.

The chemical formulae deduced from the analyses are presented in a novel and effective manner, although the reviewer is not clear why the authors, after giving data for pyrophyllite, talc and the micas on the 24 oxygen atom basis should change to the 12 atom basis in the case of the clays. Formulae employing integral numbers of oxide molecules are also attempted; mainly, one feels, as a polite gesture to the lingering ghost of Berzelius.

The final section of the paper deals with evidence bearing on the mode of origin of the clays. The authors review existing knowledge with especial reference to soils. Their own contribution is well shown in the fine series of photomicrographs illustrating the formation of bentonites by alteration of volcanic glass, and that of several members of the montmorillonite group by alteration in place of the feldspars. They stress the importance of solutions containing magnesium in the synthesis of montmorillonite. Their discussion of clay formation at Magnet Cave, Arkansas, and in the geyser region at Yellowstone will be of especial interest to volcanologists and to geologists generally.

This paper, even more than its predecessors, marks a significant stage in the advance of our knowledge of the clays. It will attract intent and critical readers from varied fields, from geology, mineralogy, ceramics, soil science and colloid chemistry. They will all be richly rewarded.

C. E. MARSHALL,
*University of Missouri,
Department of Soils, Columbia, Missouri*

REVISED LAPIDARY HANDBOOK by J. HARRY HOWARD. Published by the author, 504 Crescent Avenue, Greenville, South Carolina, 1946. Pp. 220, figs. 50, 5"×8", cloth. Price \$3.00.

The formation of the many mineralogical clubs throughout the country during the past twenty years is evidence of the greater interest in minerals and gems being taken by a rapidly increasing per cent of the general public. The members of these clubs devote much time to the collecting of specimens in the field, preparing them for exhibition or exchange, and in fashioning gem minerals for personal adornment. At present, the number of amateur and professional lapidaries in the United States and Canada is surprisingly large. Accordingly, there is great need for authoritative treatises on the art of cutting, carving, and polishing gem stones.

Revised Lapidary Handbook is a successor to the author's *Handbook for the Amateur Lapidary*, published in 1935. The number of pages has been increased by eighty, the illustrations by six. All phases of gem cutting are discussed in great detail in eighteen chapters. There are also two chapters in which useful information and the sources of lapidaries' sup-

plies are given. All chapters are by the author with the exception of Advanced Facet Cutting, which is by C. G. Waite; Artificial Coloring of Agates, by E. V. Van Amringe; and Cutting Gems by Hand, by C. C. Curtis and J. H. Howard. The Handbook will prove very helpful to all interested in the fashioning of gems.

EDWARD H. KRAUS

NEW MINERAL NAMES

Němecite

JAN VÁCLAV KAŠPAR, A new natural ferric silicate. *Rozpravy České Akad.*, **51**, No. 14, 8 pp. (1941); through *Mineralog. Abs.*, **9**, 186 (1946).

Limonite-like incrustations on pyrrhotite, associated with siderite, cronstedtite, and quartz from Chiuzbaia (Kisbánya), Roumania, gave: SiO_2 28.79, Fe_2O_3 40.20, FeO 1.00, S 0.82, H_2O (+240°) 6.97, H_2O (−240°) 22.96; sum 100.74%. The formula is $\text{H}_4\text{Fe}_2\text{Si}_2\text{O}_9 \cdot 5\text{H}_2\text{O}$, and this is confirmed by the dehydration curve. Sp. gr.=2.075, $H=2\frac{1}{2}$, isotropic with $n=1.608$. The mineral is named němecite and is believed to be the crystalline phase of the amorphous hisingerite.

DISCUSSION: Canbyite has the same composition excepting for containing less water. (Canbyite also has lower indices of refraction). X-ray study of these minerals is needed. In the absence of definite proof of a new species, this material should not have been given a new name.

MICHAEL FLEISCHER

Kladnoite

RUDOLF ROST, Supplements to the mineralogy of the burning (coal) heaps in the region of Kladno. *Rozpravy České Akad.*, **52**, no. 25, 4 pp. (1942); through *Mineralog. Abs.*, **9**, 186 (1946).

The name kladnoite is given to the organic compound phthalimide, $\text{C}_6\text{H}_4(\text{CO})_2\text{NH}$, recorded from the burning heaps at Libušín in the coal basin of Kladno, Bohemia. The monoclinic crystals are of "ruler" habit with predominant {100} and prisms {110}, {230}, {120}. Sp. gr.=1.47. Indices: $\alpha=1.501$, $\beta=1.519$, $\gamma=1.755$, $\gamma=b$, $\beta:c$ about 16° , melting point $233\text{--}235^\circ\text{C}$.

M.F.

